VOL. XXXVI. OCTOBER, 1906. No. 4.

AMERICAN

CHEMICAL JOURNAL

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN SALTS IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL, ACETONE AND BINARY MIXTURES OF THESE SOLVENTS.

[FIFTH COMMUNICATION.]

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Four papers[1] have already been published bearing upon the condition of dissolved substances in *mixed solvents*.

PART I.

INTRODUCTION.[2]

A number of investigations have been carried out in which the electrical conductivities of non-aqueous solutions have been studied, but much less has been done on the conductivities in mixtures of solvents.

[1] Jones and Lindsay: THIS JOURNAL, 28, 329 (1902). Jones and Carroll, *Ibid.*, 32, 521 (1904). Jones and Bingham: *Ibid.*, 34, 481 (1905). Jones, Lindsay and Carroll: Z. physik. Chem., 56, 129 (1906).

[2] This introduction is not a complete historical review of all that has been done upon conductivity or viscosity. In the main, only that work which pertains to mixed solvents has been taken up.

Wakeman,[1] in an elaborate investigation, measured the conductivity of a number of organic acids in mixtures of ethyl alcohol and water, in different proportions. He obtained results which showed that the conductivity became smaller as the amount of alcohol was increased. For the cases studied, the equation,

$$\frac{\Delta}{p(100-p)} = \text{constant},$$

was found to hold, where Δ is the difference between the electrical conductivity of the electrolyte in water and in the mixture, respectively, and p is the per cent of alcohol by volume.

Zelinsky and Krapiwin[2] studied the conductivities of sodium and ammonium bromides and iodides in water, methyl alcohol and a mixture of the two, containing 50 per cent of methyl alcohol; for dilutions from $v = 16$ to $v = 1024$. Their results were of a different character from those previously obtained. The conductivities in the 50 per cent mixture were considerably less than the conductivities in either water or alcohol.

A similar minimum of conductivity was obtained by Cohen,[3] working with potassium iodide in mixtures of ethyl alcohol and water. He made a study of the conductivity of this salt in mixtures containing 20, 40, 60, 80 and 99 per cent of the alcohol. The minimum was observed in the 80 per cent mixture at all dilutions greater than $v = 512$.

Cohen concluded, from the observations of Wakeman and from his own, that the relation,

$$\frac{\mu_v \text{ H}_2\text{O}}{\mu_v \text{ H}_2\text{O. Alc.}} = \text{constant},$$

holds independent of both concentration and temperature. In other words, the conductivities compared approach a limiting value at the same rate, and either the dissociation is the same in the cases compared, or conductivity is not a direct measure of dissociation in mixtures of alcohol and water. To this latter view Cohen is inclined. The work of Walker and

[1] Z. physik. Chem., 11, 49 (1893).
[2] *Ibid.*, 21, 35 (1896).
[3] *Ibid.*, 25, 31 (1898).

Hambly,[1] Hantzsch,[2] Tijmstra[3] and Roth[4] should be mentioned.

Jones and Lindsay[5] extended the work of Zelinsky and Krapiwin and Cohen, by making conductivity measurements of solutions in which the solvents were water, methyl alcohol, ethyl alcohol, propyl alcohol and binary mixtures of these solvents. The salts employed were potassium iodide, strontium iodide, ammonium bromide, cadmium bromide, lithium nitrate and ferric chloride. The result was to show that the occurrence of the minimum is more or less general. The work was, for the most part, done at 0° and 25°. Thus they were able to calculate the temperature coefficients of conductivity of the salts mentioned, in the different solvents, and could also show the influence of temperature on the minimum. They demonstrated that in some cases, although the minimum does not occur at the higher temperature, it appears at the lower. They established the fact that the effect of rise in temperature upon the minimum, is to cause it to shift towards a mixture containing a larger per cent of alcohol. They proposed to account for the conductivity minimum by assuming that each of the two associated solvents diminished the association of the other. Since, according to the theory of Dutoit and Aston, it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes, the cause of the minimum may be stated to be due to a diminution of dissociation and, consequently, a decrease in conductivity.

The above explanation was, later, strengthened by an investigation by Jones and Murray.[6] From a study of the freezing points of solutions of formic acid, acetic acid and water, and binary mixtures of these substances, they concluded that the association of one solvent is diminished by the presence of another associated solvent.

Jones and Carroll[7] studied the conductivity of cadmium iodide, sodium iodide, calcium nitrate and hydrochloric acid in

[1] J. Chem. Soc., 71, 61 (1899).
[2] Ber. d. chem. Ges., 35, 1001 (1902).
[3] Proc. Kon. Akad. de Amsterdam, 1903, p. 104.
[4] Z. physik. Chem., 42, 209 (1903).
[5] This Journal, 28, 329 (1902).
[6] *Ibid.*, 30, 193 (1903).
[7] *Ibid.*, 33, 521 (1904).

mixtures of methyl and ethyl alcohols and water. In all cases they observed the minimum at low temperatures.

Noticing the close connection between the viscosity or fluidity of a solvent, and the conductivity of electrolytes when dissolved in this solvent, they took up, in the latter part of their work, a study of this relation. That conductivity and viscosity are related is by no means a new idea, since, as early as 1856, aqueous solutions of copper sulphate were studied, in this connection, by G. Wiedemann.[1]

After an investigation of the relations between conductivity and viscosity, Jones and Carroll showed that the explanation of the minimum in conductivity offered by Jones and Lindsay was not sufficient. They proved that the phenomenon was dependent, primarily, upon the decrease in fluidity which results when the components of the solvent are mixed. They also showed that the following hypothesis holds for all cases studied by them: "The conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, etc.) are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factors of the solvent."

Formulated, this would be expressed by the equations

$$\frac{\mu_v \eta}{x} = \text{constant}, \quad \text{or} \quad \frac{\mu_v \eta}{\alpha} = \text{constant},$$

where x is the association factor and α the dissociation. These formulas become $\mu_v \eta = \text{constant}$ when $\mu_v = \mu\infty$.

This work was next continued by Jones and Bingham[2] and the relations between the conductivities and viscosities of solutions of lithium nitrate, potassium iodide and calcium nitrate, in various mixtures of acetone with water, methyl alcohol and ethyl alcohol were determined. They worked at 0° and 25° and thus were able to calculate the temperature coefficients of conductivity and of fluidity.

Their results differed from those formerly obtained by the preceding workers, in that the mixtures of acetone with the

[1] Pogg. Ann., 99, 229 (1856).
[2] This Journal, 34, 481 (1905).

alcohols showed a maximum in the conductivity of solutions of certain salts. In the case of mixtures of acetone and water, they observed the minimum previously obtained by other workers.

They measured the fluidities of mixtures of acetone with methyl alcohol, ethyl alcohol and water at 0° and 25°, and also of a few solutions of calcium nitrate at 25°. In the case of acetone and water they found a fluidity minimum, and showed that it was intimately connected with the minimum in conductivity. In the mixtures of acetone and the alcohols they found that the fluidity values obeyed the law of averages. From this fact they concluded that acetone and the alcohols do not form more complex molecular aggregations when mixed, than were originally present before mixing.

After a comprehensive study of all the factors that could influence conductivity, they came to the conclusion that the maximum in conductivity obtained by them was due to a *change in the dimensions of the atmospheres about the ions.* They also showed that the conclusion of Jones and Carroll, that conductivity is proportional to dissociation, was incomplete in that it did not take into consideration possible changes in the size of the ionic spheres.

Jones and Bingham, in their work, showed that the normal curve for viscosities is the hyperbola, and that the normal curve for fluidity is a straight line.

Using the viscosity data of Thorpe and Rodger, Bingham[1] calculated the corresponding values of fluidity for a number of solvents, and plotted the results in curves. He has shown that fluidities alone should be additive and that the normal viscosity curve is a hyperbola, a fact similar to that found by Jones and Bingham.

Some of the recent work on conductivity in non-aqueous solutions should be mentioned. Godlewski[2] has determined the conductivity of a few weak organic acids in ethyl alcohol and in mixtures of ethyl alcohol and water. In all the cases studied he found that Ostwald's dilution law holds. He also

[1] THIS JOURNAL, 35, 195 (1906).
[2] J. Chim. Phys. 3, 393 (1905).

determined the conductivity of acetic acid in amyl alcohol and found that it decreases with increasing dilution, until a concentration of about 0.5 N was reached, when it has a minimum value. The dielectric constants of the solutions were found to increase with an increase in dilution.

Dutoit and Levier[1] have determined the conductivity of a few salts in acetone at dilutions as great as $v = 100{,}000$. They found that the conductivity of the salts became constant at the highest dilutions; and that Kohlrausch's law,

$$\mu\infty = c + a,$$

holds in acetone, where c represents the velocity of the cation and a that of the anion.

Walden[2] has just published the third part of his investigations on organic solvents. This includes work in methyl and ethyl alcohols and glycol, a number of aldehydes, acid anhydrides and chlorides, organic esters and inorganic acids, nitriles, sulphocyanides and mustard oils, nitro and nitroso compounds, ketones, epichlorhydrin, pyridine, and certain mixtures of some of these solvents.

He finds that for the same electrolyte—$N(C_2H_5)_4I$—in all of the solvents that were studied, temperature being constant (25°), the product of $\mu\infty$ times the internal friction is a constant. The product of the internal friction and $\mu\infty$ for organic solvents was shown to be independent of the nature of the solvent and of the temperature.

In reference to the relation pointed out by Jones and Carroll, to which Walden refers,[3] it should be stated that Jones and Carroll tested this relation for only a limited number of solvents. For these it held fairly satisfactorily. The concentrations used were the simplest possible, *i. e.*, a molecule of the substance in so many molecules of the solvent. In their calculations the association factors of the several solvents were not introduced, since this was the very point to be tested.

Our work was undertaken as an extension of the work of Jones and Carroll on the one hand, and of that of Jones and

[1] J. Chim. Phys. **3**, 435 (1905).
[2] Z. physik. Chem., **55**, 207 (1906).
[3] *Ibid.*, **55**, 213 (1906).

Bingham on the other. It will be recalled that Jones and Carroll investigated the relations between conductivity and viscosity of salts in water, methyl and ethyl alcohols and binary mixtures of these solvents; while Jones and Bingham pointed out the relation between conductivity and viscosity of certain salts in mixtures of acetone with methyl and ethyl alcohols and water.

We have worked with water, methyl alcohol, ethyl alcohol, acetone and 17 different binary mixtures of these solvents. The salts studied were lithium bromide and cobalt chloride.

PART II.

EXPERIMENTAL.

Apparatus.

(*a*) *Conductivity.*—The Kohlrausch method of measuring conductivity, with a Wheatstone bridge, telephone receiver and induction coil, was employed. The bridge wire was of "manganin" and was calibrated before beginning the work by the method of Strouhal and Barus.[1]

The resistance coils, manufactured by Leeds & Co., were tested and found to be accurate to within 0.04 per cent.

The conductivity cells were of the form used by Jones and Bingham.[2] In order to work with the alcohols and acetone, it was necessary to use cells of this form. They were made of hard glass, with ground-glass stoppers. The glass tubes carrying the platinum electrodes were sealed into both the upper and lower walls of the stopper. By using such cells, the presence of rubber or wax, which would be dissolved by the solutions, was avoided. They also prevent evaporation of the more volatile solvents, and protect the anhydrous alcohols and acetone from the moisture of the baths and air.

The electrodes were treated in the manner recommended by Whetham.[3] They were first coated with platinum black and then heated in the flame of a blast-lamp. Electrodes covered with platinum black absorb a small amount of salt from the

[1] Wied. Ann., 10, 326 (1880).
[2] This Journal, 34, 493 (1905).
[3] Phil. Trans., 94 [A], 321 (1900).

solution and give up some of it again when water, or a more dilute solution is placed in the cell. The gray platinum formed by the heating process does not absorb an appreciable amount of salt, and the oxidizing action of platinum black is also avoided by this treatment.

The zero bath consisted of an inner and outer vessel. The inner vessel and the space between the two were filled with finely crushed, pure ice, moistened with distilled water. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine, or a Rabe water turbine. The Ostwald thermoregulator was used. The thermometers employed were accurate to a tenth of a degree. Burettes and flasks were carefully calibrated, according to the method of Morse and Blalock.[1]

(*b*) *Viscosity.*—The apparatus used was exactly of the form described by Ostwald and Luther.[2] A fixed volume of the liquid, the viscosity of which was to be measured, was introduced into the viscometer. The liquid was raised to the mark above the bulb by means of air pressure, the air being dried with calcium chloride, or with concentrated sulphuric acid. The pressure was then released by means of a Mohr pinch-cock on a thick-walled rubber tube. The time of flow through the capillary tube was determined by means of a stop-watch, reading to two-tenths of a second.

We are indebted to Mr. Arthur C. Macy, jeweler, for the loan of a Waltham stop-watch.

In order to calculate the viscosity, it is necessary to measure the specific gravity of the solution. For this purpose we used the pycnometer employed by Jones and Bingham[3] in their work. The pycnometer was so constructed as to allow the large expansion of the alcohols and acetone and avoid loss by evaporation.

A large battery jar, filled with finely crushed ice moistened with water, was used for the zero bath. The ice was frequently renewed to keep the temperature constant. For the

[1] THIS JOURNAL, 16, 479 (1894).
[2] Physiko.-chemische Messungen, II. Aufl., p. 260.
[3] THIS JOURNAL, 34, 495 (1905).

25° bath a beaker holding 5 liters was used. The bath was stirred by means of a hot-air engine, the temperature being kept at 25°. It did not vary more than a tenth of a degree.

Solvents.

Water.—The water used in this work was purified according to the following method: Ordinary distilled water was first distilled from potassium bichromate and sulphuric acid. This water was redistilled from acidified potassium bichromate and then from barium hydroxide. Water thus purified gave a conductivity of 1×10^{-6} at 0° and from $1.5\text{–}2.0 \times 10^{-6}$ at 25°.

Methyl Alcohol.—The methyl alcohol used was the best commercial article which could be obtained. It was first boiled with calcium oxide for several days, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate, using a Linnemann fractionating head. Care was always taken to keep it free from moisture. The first and last portions of the distillate were discarded. The mean value of the conductivity was 1.1×10^{-6} at 0° and 2×10^{-6} at 25°.

Ethyl Alcohol.—The ethyl alcohol was the best article commercially obtainable, and was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 0.6×10^{-6} at 0° and 1.5×10^{-6} at 25°.

Acetone.—The acetone was dried over fused calcium chloride for weeks and distilled with a Linnemann fractionating head. Its conductivity was 0.4×10^{-6} at 0° and 0.6×10^{-6} at 25°.

Solutions.

In making up mixtures of solvents, "x" cc. of an alcohol or of acetone were diluted to 100 cc. Such a solution was designated as a mixture of "x per cent alcohol" or "x per cent acetone." Since acetone has a large coefficient of expansion, it was necessary to make up the mixtures at the same temperature (18°). The alcohol or acetone was always brought to this temperature before making up the mixture.

In making up the mother solution the exact amount of the salt was weighed into a measuring flask and, after addition of

a portion of the solvent, the substance was dissolved and the flask filled to the mark. Since heat was generated and there was a rise in temperature, the solution was brought to the designated temperature before diluting to the mark. The various concentrations were obtained by successive dilution, the mother solution being the starting point. Where the quantity to be used was too small to be measured with accuracy, one of the intermediate solutions was taken as a starting point for further dilution.

Conductivity Measurements.

In all determinations of conductivity from 3 to 5 different resistances were used. The values for the molecular conductivity (μ_v), given in the tables, are, therefore, the mean of several determinations. The determination of the cell constants was carried out by the method employed by Jones and West.[1] Cells calibrated in this manner gave very accurate results. The constants were checked at frequent intervals. After being used the cells were not allowed to remain in contact with the solution, because small quantities of salt are absorbed by the electrodes. Nor were they allowed to remain empty after being dried out with alcohol and ether, since acetic acid is formed by the action of the platinum on the alcohol and ether in the presence of air, but they were always filled with pure distilled water when not in use.

Solutions of potassium chloride, 0.02 N and 0.002 N, were used in determining the cell constants. The conductivity of the former was taken as 129.7, at 25° ; 136.5 at 25° being taken as the value of μ_v for the 0.002 N solution of potassium chloride.

In the following tables v = number of liters of solution containing a gram-molecular weight of the salt ; μ_v 0° = molecular conductivity at 0° ; μ_v 25° = molecular conductivity at 25°.

The temperature coefficients are obtained by dividing the increase in the conductivity per degree by the conductivity at the lower temperature. The formula, that was applied, is

[1] This Journal, 34, 357 (1905).

$$\frac{\mu_v\ 25^\circ - \mu_v\ 0^\circ}{25} \cdot \frac{1}{\mu_v\ 0^\circ}.$$

LITHIUM BROMIDE.

The lithium bromide used in this work was obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 159°, after which it was kept in a desiccator. Whenever the salt was exposed to the air the operation of drying to constant weight was repeated.

Table I.—Conductivity of Lithium Bromide in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	42.09	76.17	0.0324
5	45.33	83.33	0.0335
10	47.25	86.09	0.0329
50	51.43	95.62	0.0344
100	51.92	96.41	0.0342
200	53.27	99.51	0.0347
400	53.71	100.34	0.0347
800	55.45	104.81	0.0356
1600	56.12	106.23	0.0357

Table II.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	24.46	49.86	0.0415
5	26.57	54.90	0.0426
10	27.52	57.46	0.0435
50	30.04	63.69	0.0448
100	30.50	64.78	0.0450
200	31.24	66.25	0.0448
400	31.65	66.65	0.0442
800	32.87	68.83	0.0438
1600	33.07	69.24	0.0437

Table III.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	18.42	37.01	0.0404
5	20.57	41.58	0.0408
10	21.71	43.99	0.0410
50	24.24	49.46	0.0416
100	24.40	50.27	0.0424
200	25.16	51.74	0.0423
400	25.96	53.24	0.0420
800	26.42	54.48	0.0425
1600	26.91	55.15	0.0420

Table IV.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	19.51	33.66	0.0290
5	21.67	38.31	0.0307
10	23.50	41.99	0.0314
50	27.05	48.68	0.0320
100	27.73	49.98	0.0321
200	28.92	52.29	0.0323
400	29.55	53.56	0.0325
800	30.22	55.29	0.0332
1600	31.35	57.59	0.0335

Table V.—Conductivity of Lithium Bromide in Methyl Alcohol at 0° and 25°.

v.	μ_v 0.	μ_v 25°.	Temperature coefficients.
2	22.02	31.35	0.0169
5	30.55	42.57	0.0157
10	35.92	50.21	0.0159
50	46.48	64.92	0.0159
100	49.36	69.19	0.0161
200	52.51	73.62	0.0161
400	55.18	78.25	0.0167
800	57.45	82.56	0.0175
1600	57.63	83.64	0.0181

Table VI.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	42.09	24.46	18.42	19.51	22.02
5	45.33	26.57	20.57	21.67	30.55
10	47.25	27.52	21.71	23.50	35.92
50	51.43	30.04	24.24	27.05	46.48
100	51.92	30.50	24.40	27.73	49.36
200	53.27	31.24	25.16	28.92	52.51
400	53.71	31.65	25.96	29.55	55.18
800	55.45	32.87	26.42	30.22	57.45
1600	56.12	33.07	26.91	31.35	57.63

Table VII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	76.17	49.86	37.01	33.66	31.35
5	83.33	54.90	41.58	38.31	42.57
10	86.09	57.46	43.99	41.99	50.21
50	95.62	63.69	49.46	48.68	64.92
100	96.41	64.78	50.27	49.98	69.19
200	99.51	66.25	51.74	52.29	73.62
400	100.34	66.65	53.24	53.56	78.25
800	104.81	68.83	54.48	55.29	82.56
1600	106.23	69.24	55.15	57.59	83.64

Table VIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Methyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	0.0324	0.0415	0.0404	0.0290	0.0169
5	0.0335	0.0426	0.0408	0.0307	0.0157
10	0.0329	0.0435	0.0410	0.0314	0.0159
50	0.0344	0.0448	0.0416	0.0320	0.0159
100	0.0342	0.0450	0.0424	0.0321	0.0161
200	0.0347	0.0448	0.0423	0.0323	0.0161
400	0.0347	0.0442	0.0420	0.0325	0.0167
800	0.0356	0.0438	0.0425	0.0332	0.0175
1600	0.0357	0.0437	0.0420	0.0335	0.0181

Tables I. to VIII. (Figs. I. and II.) show that lithium bromide, in mixtures of methyl alcohol and water, gives a pronounced minimum in conductivity. The minimum is more marked at 0° than at 25°. At 25° the minimum occurs in the 75 per cent mixture up to $v = 100$. Beyond this dilution the

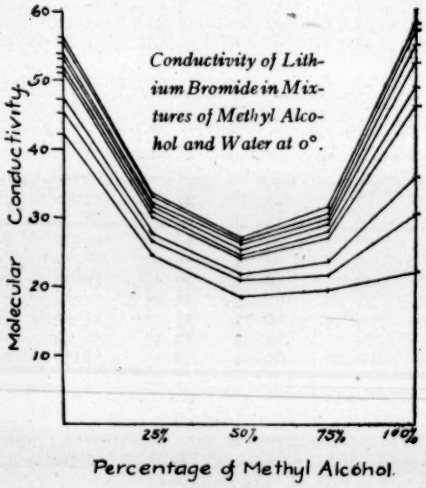


Fig. I.

minimum occurs solely in the 50 per cent mixture. At 0° the minimum appears in the 50 per cent mixture alone. We also notice that at 0° the values of μ_v for the pure methyl alcohol at the higher dilutions, exceed the values of μ_v for the corresponding aqueous solutions.

These points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.

The temperature coefficients of conductivity increase with the dilution, and they are also greater in the mixtures than in

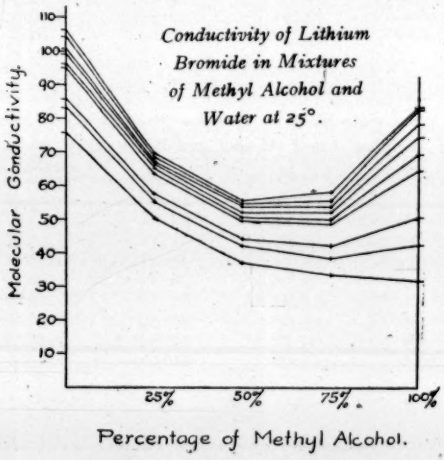


Fig. II.

the pure solvents, the maximum appearing in the 25 per cent mixture. The temperature coefficients of conductivity of salts in water generally increase with the dilution, as Jones[1] has pointed out in a recent article.

[1] This Journal, 35, 445 (1906).

Table IX.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	17.82	41.21	0.0525
5	18.92	45.03	0.0552
10	19.66	47.05	0.0557
50	21.60	52.52	0.0572
100	21.67	52.58	0.0570
200	22.09	54.37	0.0584
400	22.50	54.41	0.0567
800	24.51	56.46	0.0521
1600	25.72	57.10	0.0448

Table X.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	11.70	27.50	0.0540
5	12.48	29.51	0.0546
10	12.62	31.41	0.0595
50	13.71	35.41	0.0633
100	13.98	36.12	0.0633
200	14.34	37.26	0.0639
400	14.96	38.39	0.0626
800	15.77	39.94	0.0613
1600	16.06	40.01	0.0596

Table XI.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	9.20	18.96	0.0424
5	10.55	22.11	0.0438
10	11.59	24.26	0.0437
50	11.87	25.62	0.0463
100	12.14	26.29	0.0466
200	12.77	27.66	0.0466
400	13.13	28.62	0.0472
800	13.62	29.78	0.0474
1600	13.83	29.91	0.0465

Table XII.—Conductivity of Lithium Bromide in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	6.11	10.18	0.0266
5	8.67	14.00	0.0246
10	10.55	17.22	0.0253
50	14.40	23.28	0.0247
100	15.69	25.57	0.0252
200	17.29	28.26	0.0254
400	18.55	30.32	0.0254
800	19.71	31.73	0.0244
1600	20.79	33.36	0.0242

Table XIII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Ethyl Alcohol and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	42.09	17.82	11.70	9.20	6.11
5	45.33	18.92	12.48	10.55	8.67
10	47.25	19.66	12.62	11.59	10.55
50	51.43	21.60	13.71	11.87	14.40
100	51.92	21.67	13.98	12.14	15.69
200	53.27	22.09	14.34	12.77	17.29
400	53.71	22.50	14.96	13.13	18.55
800	55.45	24.51	15.77	13.62	19.71
1600	56.12	25.72	16.06	13.83	20.79

Table XIV.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Ethyl Alcohol and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	76.17	41.21	27.50	18.96	10.18
5	83.83	45.03	29.51	22.11	14.00
10	86.09	47.05	31.41	24.26	17.22
50	95.62	52.52	35.41	25.62	23.28
100	96.41	52.58	36.12	26.29	25.57
200	99.51	54.37	37.26	27.66	28.26
400	100.34	54.41	38.39	28.62	30.32
800	104.81	56.46	39.94	29.78	31.73
1600	106.23	57.10	40.01	29.91	33.36

Table XV.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Ethyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
2	0.0324	0.0525	0.0540	0.0424	0.0266
5	0.0335	0.0552	0.0546	0.0438	0.0246
10	0.0329	0.0557	0.0595	0.0437	0.0253
50	0.0344	0.0572	0.0633	0.0463	0.0247
100	0.0342	0.0570	0.0633	0.0466	0.0252
200	0.0347	0.0584	0.0639	0.0466	0.0254
400	0.0347	0.0567	0.0626	0.0472	0.0254
800	0.0356	0.0521	0.0613	0.0474	0.0244
1600	0.0357	0.0448	0.0596	0.0465	0.0242

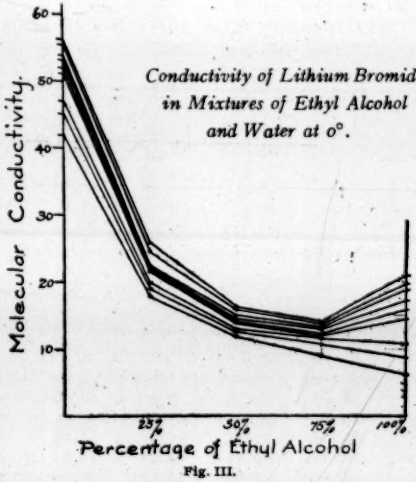


Fig. III.

Tables IX. to XV. (Figs. III. and IV.) show that lithium bromide, in mixtures of ethyl alcohol and water, also gives a

minimum in conductivity. At high concentrations the minimum does not appear, either at 0° or at 25°. At both temperatures the minimum appears only in the 75 per cent mixture. At 0° the minimum begins with $v = 50$, at 25° it be-

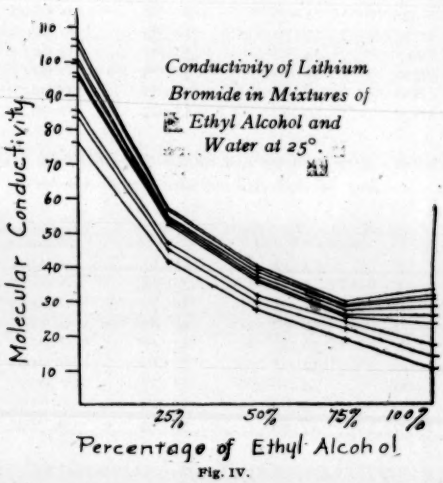


Fig. IV.

gins at $v = 200°$. It is to be noticed that the minimum is more marked at the lower temperature, being very slight at 25°.

The temperature coefficients in ethyl alcohol are almost constant. This same fact was found by Jones and Bingham[1] in the case of calcium nitrate. The temperature coefficients are greater in the mixtures than in the pure solvents, the maximum appearing in the 50 per cent mixture.

[1] THIS JOURNAL, 34, 529 (1905).

Table XVI.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	8.59	13.51	0.0229
5	12.55	19.08	0.0208
10	15.17	22.97	0.0206
50	21.07	31.56	0.0199
100	22.70	34.55	0.0209
200	24.50	37.61	0.0214
400	26.08	40.03	0.0214
800	26.94	41.82	0.0221
1600	29.08	45.07	0.0220

Table XVII.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	12.22	18.37	0.0201
5	17.38	25.54	0.0188
10	21.03	30.72	0.0184
50	28.69	41.81	0.0183
100	30.42	44.48	0.0185
200	32.95	48.86	0.0193
400	34.76	51.31	0.0190
800	35.83	53.29	0.0195
1600	37.53	55.74	0.0194

Table XVIII.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
2	16.46	24.22	0.0188
5	23.34	33.38	0.0172
10	27.71	39.60	0.0171
50	37.02	52.80	0.0170
100	38.96	55.92	0.0174
200	41.64	60.03	0.0176
400	44.21	63.76	0.0177
800	46.51	66.73	0.0174
1600	49.57	71.37	0.0176

Table XIX.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Ethyl Alcohol at 0°.

v.	C_2H_5OH.	25 per cent CH_3OH.	50 per cent CH_3OH.	75 per cent CH_3OH.	CH_3OH.
2	6.11	8.59	12.22	16.46	22.02
5	8.67	12.55	17.38	23.34	30.55
10	10.55	15.17	21.03	27.71	35.92
50	14.40	21.07	28.69	37.02	46.48
100	15.69	22.70	30.42	38.96	49.36
200	17.27	24.50	32.95	41.64	52.51
400	18.55	26.08	34.76	44.21	55.18
800	19.71	26.94	35.83	46.51	57.45
1600	20.79	29.08	37.53	49.57	57.63

Table XX.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Methyl Alcohol and Ethyl Alcohol at 25°.

v.	C_2H_5OH.	25 per cent CH_3OH.	50 per cent CH_3OH.	75 per cent CH_3OH.	CH_3OH.
2	10.18	13.51	18.37	24.22	31.35
5	14.00	19.08	25.54	33.38	42.57
10	17.22	22.97	30.72	39.60	50.21
50	23.28	31.56	41.81	52.80	64.92
100	25.57	34.55	44.48	55.92	69.19
200	28.26	37.61	48.86	60.03	73.62
400	30.32	40.03	51.31	63.76	78.25
800	31.73	41.82	53.29	66.73	82.56
1600	33.36	45.07	55.74	71.37	83.64

Table XXI.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Methyl Alcohol and Ethyl Alcohol from 0° to 25°.

v.	C_2H_5OH.	25 per cent CH_3OH.	50 per cent CH_3OH.	75 per cent CH_3OH.	CH_3OH.
2	0.0266	0.0229	0.0201	0.0188	0.0169
5	0.0246	0.0208	0.0188	0.0172	0.0157
10	0.0253	0.0206	0.0184	0.0171	0.0159
50	0.0247	0.0199	0.0183	0.0170	0.0159
100	0.0252	0.0209	0.0185	0.0174	0.0161
200	0.0254	0.0214	0.0193	0.0176	0.0161
400	0.0254	0.0214	0.0190	0.0177	0.0167
800	0.0244	0.0221	0.0195	0.0174	0.0175
1600	0.0242	0.0220	0.0194	0.0176	0.0181

Tables XVI. to XXI. (Figs. V. and VI.) show that lithium bromide, in mixtures of methyl and ethyl alcohols, gives no minimum in conductivity. In fact, the conductivity values

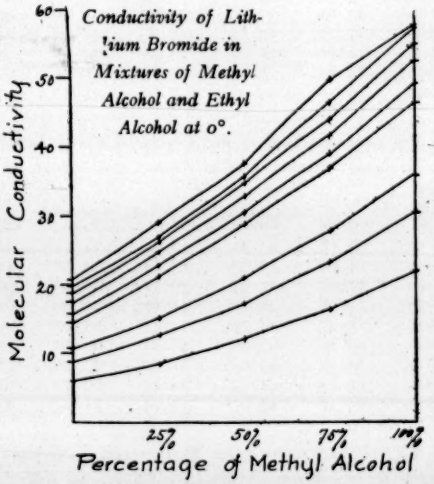


Fig. V.

for the solutions in the mixed solvent approach the mean value of the conductivities in the pure solvents. The conductivity curves at the high concentrations show a slight sagging at both temperatures, but beyond $v = 50$ the curves are nearly straight lines.

This same fact has been observed by others[1] working with mixtures of methyl and ethyl alcohols. The temperature coefficients obey, approximately, the law of averages.

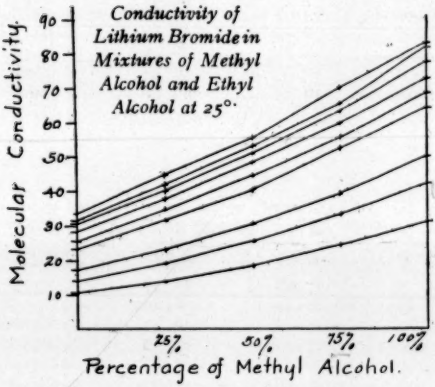


Fig. VI.

Table XXII.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.58	56.23	0.0415
10	28.82	59.71	0.0429
50	31.49	65.64	0.0434
100	31.60	65.82	0.0433
200	32.29	67.88	0.0441
400	32.98	68.69	0.0433
800	35.18	70.25	0.0399
1600	35.70	71.47	0.0401

[1] Jones and Lindsay: *Loc. cit.* Jones and Carroll: *Loc. cit.*

Table XXIII.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	20.37	41.82	0.0421
10	21.70	45.16	0.0432
50	24.81	51.95	0.0437
100	25.03	52.46	0.0438
200	26.10	54.64	0.0437
400	26.81	56.44	0.0442
800	27.07	57.54	0.0430
1600	28.34	59.28	0.0437

Table XXIV.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	17.40	31.47	0.0323
10	20.40	36.49	0.0315
50	25.76	46.77	0.0326
100	27.29	49.87	0.0331
200	28.87	52.87	0.0332
400	30.10	55.53	0.0338
800	30.20	56.46	0.0348
1600	31.65	61.10	0.0372

Table XXV.—Conductivity of Lithium Bromide in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	9.35	10.82	0.00629
10	11.91	14.08	0.00729
50	22.36	26.77	0.00789
100	28.86	34.52	0.00784
200	37.33	47.45	0.01080
400	48.28	57.96	0.00802
800	59.42	72.16	0.00858
1600	70.89	85.90	0.00847

Table XXVI.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	45.33	27.58	20.37	17.40	9.35
10	47.25	28.82	21.70	24.00	11.91
50	51.43	31.49	24.81	25.76	22.36
100	51.92	31.60	25.03	27.29	28.86
200	53.27	32.29	26.10	28.87	37.33
400	53.71	32.98	26.81	30.10	48.28
800	55.45	35.18	27.07	30.20	59.42
1600	56.12	35.71	28.34	31.65	70.89

Table XXVII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	83.33	56.23	41.82	31.47	10.82
10	86.09	59.71	45.16	36.49	14.80
50	95.61	65.64	51.95	46.77	26.77
100	96.41	65.82	52.46	49.87	34.52
200	99.51	67.88	54.64	52.87	47.45
400	100.34	68.69	56.44	55.53	57.96
800	104.81	70.25	57.54	56.46	72.16
1600	106.23	71.47	59.28	61.10	85.90

Table XXVIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0335	0.0415	0.0421	0.0323	0.00629
10	0.0329	0.0429	0.0432	0.0315	0.00729
50	0.0344	0.0434	0.0437	0.0326	0.00789
100	0.0342	0.0433	0.0438	0.0331	0.00784
200	0.0347	0.0441	0.0437	0.0332	0.01080
400	0.0347	0.0433	0.0442	0.0338	0.00802
800	0.0356	0.0399	0.0430	0.0348	0.00858
1600	0.0357	0.0401	0.0437	0.0372	0.00847

Tables XXII. to XXVIII. (Figs. VII. and VIII.) for lithium bromide, in mixtures of acetone and water, give the minimum which is exhibited in mixtures of the alcohols and water

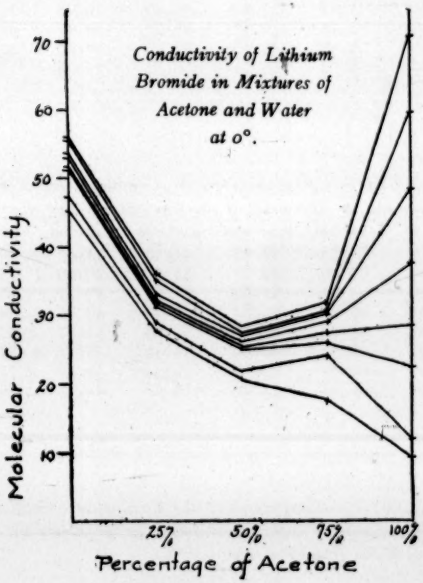


Fig. VII.

under similar circumstances. The minimum is more marked at the lower temperature. The curves diverge from each other rapidly between the 75 per cent mixture and pure ace-

tone, at both temperatures. This seems to indicate that the addition of small amounts of water greatly increases the dissociation. It is also to be noticed that, at the lower temperature, the values of μ_v for the pure acetone at the higher dilu-

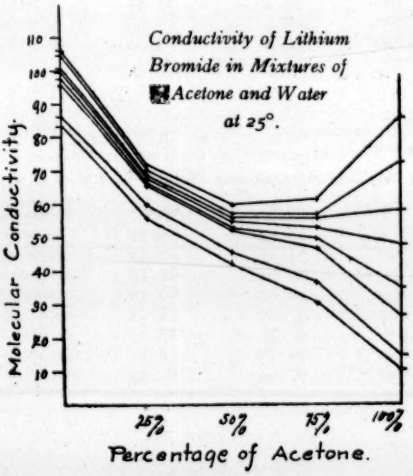


Fig. VIII.

tions exceed those of μ_v for the corresponding water solutions. A similar phenomenon was noticed in the methyl alcohol and water solutions.

In pure acetone the temperature coefficients increase with the dilution. In the mixtures the increase is very small.

Table XXIX.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	29.65	40.04	0.0140
10	35.03	47.57	0.0143
50	46.71	63.44	0.0143
100	49.68	67.40	0.0142
200	53.28	73.81	0.0154
400	56.45	78.11	0.0153
800	58.91	81.55	0.0154
1600	60.38	83.53	0.0153

Table XXX.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.99	35.37	0.0105
10	34.27	42.32	0.00939
50	48.65	61.77	0.0108
100	52.67	68.29	0.0118
200	57.69	74.13	0.0114
400	61.74	79.77	0.0117
800	64.70	85.57	0.0129
1600	67.02	89.45	0.0134

Table XXXI —Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	23.36	30.06	0.0115
10	29.77	38.15	0.0112
50	48.45	61.89	0.0111
100	55.00	70.87	0.0115
200	62.74	80.63	0.0114
400	72.25	91.17	0.0105
800	82.20	100.28	0.0088
1600	84.15	106.14	0.0104

Table XXXII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	30.55	29.65	27.99	23.36	9.35
10	35.92	35.03	34.27	29.77	11.91
50	46.48	46.71	48.65	48.45	22.36
100	49.36	49.68	52.67	55.00	28.86
200	52.51	53.28	57.69	62.74	37.33
400	55.18	56.45	61.74	72.25	48.28
800	57.45	58.91	64.70	82.20	59.42
1600	57.63	60.38	67.02	84.15	70.89

Table XXXIII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	42.57	40.04	35.37	30.06	10.82
10	50.21	47.57	42.32	38.15	14.08
50	64.92	63.44	61.77	61.89	26.77
100	69.19	67.40	68.29	70.87	34.52
200	73.62	73.81	74.13	80.63	47.45
400	78.25	78.11	79.77	91.17	57.96
800	82.56	81.55	85.57	100.28	72.16
1600	83.64	83.53	89.45	106.14	85.90

Table XXXIV.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0157	0.0140	0.0105	0.0115	0.00629
10	0.0159	0.0143	0.00939	0.0112	0.00729
50	0.0159	0.0143	0.0108	0.0111	0.00789
100	0.0161	0.0142	0.0118	0.0115	0.00784
200	0.0161	0.0154	0.0114	0.0114	0.01080
400	0.0167	0.0153	0.0117	0.0105	0.00802
800	0.0175	0.0154	0.0129	0.0088	0.00858
1600	0.0181	0.0153	0.0134	0.0104	0.00847

Tables XXIX. to XXXIV. (Figs. IX. and X.) for lithium bromide, in mixtures of acetone and methyl alcohol, give a maximum in conductivity in the 75 per cent mixture at both

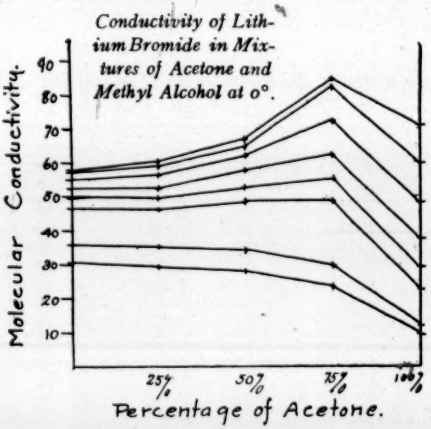


Fig. IX.

temperatures. The maximum is increased by rise in temperature. This same phenomenon was found by Jones and Bing-

ham, working with lithium nitrate in mixtures of acetone and methyl alcohol. It will be recalled that we obtained a mini-

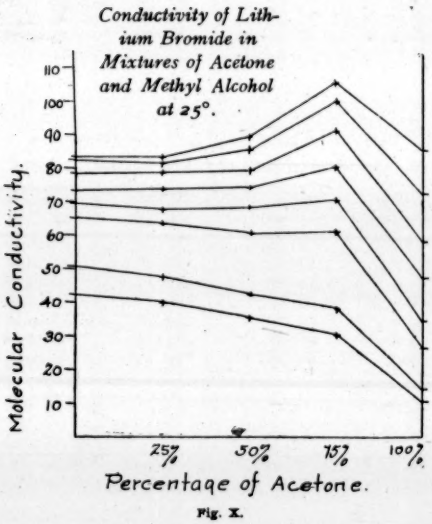


Fig. X.

mum conductivity with this salt in mixtures of the alcohols and water.

Table XXXV.—Conductivity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	11.80	16.94	0.0174
10	14.72	20.91	0.0168
50	21.70	31.00	0.0171
100	23.70	34.38	0.0180
200	26.38	38.27	0.0180
400	28.28	41.74	0.0190
800	28.88	42.97	0.0195
1600	29.21	44.24	0.0206

Table XXXVI.—Conductivity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.70	19.38	0.0122
10	19.23	25.75	0.0135
50	30.25	39.36	0.0120
100	34.50	45.12	0.0123
200	39.20	52.76	0.0138
400	43.83	59.26	0.0141
800	46.92	64.33	0.0148
1600	50.98	71.22	0.0159

Table XXXVII.—Conductivity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.48	18.07	0.00992
10	19.16	23.23	0.00850
50	33.20	40.08	0.00829
100	39.32	48.94	0.00978
200	47.31	58.01	0.00905
400	55.55	68.28	0.00917
800	61.20	77.57	0.01070
1600	66.28	83.36	0.01030

Table XXXVIII.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	8.67	11.8	14.70	14.48	9.35
10	10.55	14.72	19.23	19.16	11.91
50	14.40	21.70	30.25	33.20	22.36
100	15.69	23.70	34.50	39.32	28.86
200	17.29	26.38	39.20	47.31	37.33
400	18.55	28.28	43.83	55.55	48.28
800	19.71	28.88	46.92	61.20	59.42
1600	20.79	29.21	50.98	66.28	70.89

Table XXXIX.—Comparison of the Conductivities of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.00	16.94	19.38	18.07	10.82
10	17.22	20.91	25.75	23.23	14.08
50	23.28	31.00	39.36	40.08	26.77
100	25.57	34.38	45.12	48.94	34.52
200	28.26	38.27	52.76	58.01	47.45
400	30.32	41.74	59.26	68.28	57.96
800	31.73	42.97	64.33	77.57	72.16
1600	33.36	44.24	71.22	83.36	85.90

Table XL.—Comparison of the Temperature Coefficients of Conductivity of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0246	0.0174	0.0122	0.00992	0.00629
10	0.0253	0.0168	0.0135	0.00850	0.00729
50	0.0247	0.0171	0.0120	0.00829	0.00789
100	0.0252	0.0180	0.0123	0.00978	0.00784
200	0.0254	0.0180	0.0138	0.00905	0.01080
400	0.0254	0.0190	0.0141	0.00917	0.00802
800	0.0244	0.0195	0.0148	0.01070	0.00858
1600	0.0242	0.0206	0.0159	0.01030	0.00847

Tables XXXV. to XL. (Figs. XI. and XII.) for lithium bromide, in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this salt

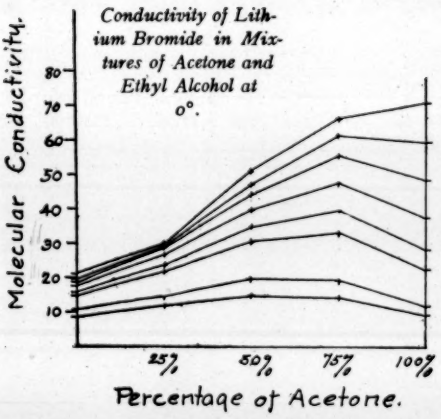


Fig. XI.

in mixtures of acetone and methyl alcohol. The values for μ_v in acetone are greater than the corresponding values in the pure ethyl alcohol at practically all dilutions.

The temperature coefficients increase slightly with the increase in dilution. The values are highest in ethyl alcohol,

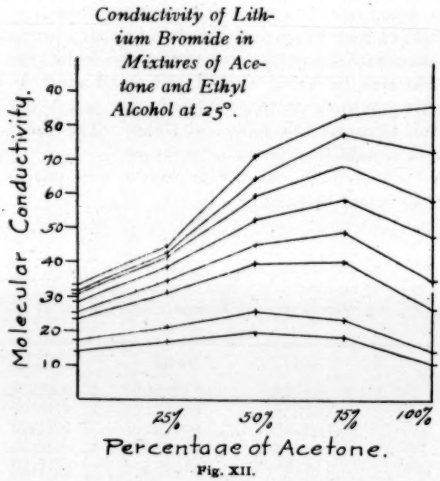


Fig. XII.

from which there is a regular gradation to the values of pure acetone.

COBALT CHLORIDE.

The cobalt chloride used in this work was obtained from Kahlbaum. No appreciable impurity could be detected. This salt cannot be dehydrated in contact with the air, and special precautions must be taken to prevent the formation of the oxychloride. The salt containing 6 molecules of water was first placed over concentrated sulphuric acid, in a vacuum desiccator, for several days. It was thus deprived of part of its water of crystallization. It was then placed in an air-bath and dried at 140°–150°, in a stream of dry hydrochloric acid gas. The salt was subsequently kept in a vacuum desiccator over sul-

phuric acid and potassium hydroxide. It gave no test for free hydrochloric acid, and possessed a pale, sky-blue color.

Cobalt chloride, dissolved in methyl and ethyl alcohols and acetone, gives rise to a number of color phenomena. These changes have been extensively studied by many investigators. Spectroscopic observations concerning the color changes of cobalt chloride in water, methyl and ethyl alcohol, acetone and binary mixtures of these solvents, are now being carried out in this laboratory by Jones and Uhler. The results of this work will be published in the near future.

Hydrolysis probably comes into play, to some extent, in the more dilute water solutions.

Table XLI.—Conductivity of Cobalt Chloride in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	86.42	156.36	0.0324
50	104.31	189.27	0.0326
100	109.27	197.41	0.0322
200	113.73	213.40	0.0350
400	115.87	219.63	0.0358
800	116.71	220.04	0.0354
1600	117.40	221.50	0.0355

Table XLII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	43.97	92.35	0.0440
50	52.02	110.24	0.0447
100	52.39	112.95	0.0462
200	57.20	126.60	0.0485
400	57.99	125.17	0.0463
800	60.14	127.46	0.0447
1600	61.98	133.98	0.0472

Table XLIII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	32.94	65.85	0.0400
50	39.96	82.44	0.0425
100	41.39	85.58	0.0427
200	44.95	92.90	0.0427
400	46.15	96.35	0.0435
800	48.51	100.54	0.0429
1600	51.40	104.19	0.0411

Table XLIV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	27.40	49.58	0.0324
50	37.45	61.58	0.0258
100	38.07	66.17	0.0296
200	43.16	76.01	0.0304
400	45.54	77.82	0.0283
800	48.55	80.51	0.0263
1600	51.39	84.39	0.0257

Table XLV.—Conductivity of Cobalt Chloride in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	33.46	41.78	0.00995
50	51.76	65.22	0.01040
100	60.89	76.08	0.00998
200	70.45	87.37	0.00961
400	75.64	99.96	0.01280
800	86.57	117.18	0.01410
1600	95.54	133.33	0.01580

Table XLVI.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	86.42	43.97	32.94	27.40	33.46
50	104.31	52.02	39.96	37.45	51.76
100	109.27	52.39	41.39	38.07	60.89
200	113.73	57.20	44.95	43.16	70.45
400	115.87	57.99	46.15	45.54	75.64
800	116.71	60.14	48.51	48.55	86.57
1600	117.40	61.98	51.40	51.39	95.54

Table XLVII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	156.36	92.35	65.85	49.58	41.780
50	189.27	110.24	82.44	61.58	65.220
100	197.41	112.95	85.58	66.17	76.080
200	213.40	126.60	92.90	76.01	87.370
400	219.63	125.17	96.35	77.82	99.960
800	220.04	127.46	100.54	80.51	117.18
1600	221.50	133.98	104.19	84.39	133.33

Table XLVIII.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0324	0.0440	0.0400	0.0324	0.00995
50	0.0326	0.0447	0.0425	0.0258	0.01040
100	0.0322	0.0462	0.0427	0.0296	0.00998
200	0.0350	0.0485	0.0427	0.0304	0.00961
400	0.0358	0.0463	0.0435	0.0283	0.01280
800	0.0354	0.0447	0.0429	0.0263	0.01410
1600	0.0355	0.0472	0.0411	0.0257	0.01580

Tables XLI. to XLVIII. (Figs. XIII. and XIV.) for cobalt chloride, in mixtures of methyl alcohol and water, show a minimum in conductivity at both temperatures. It should be noticed that the minimum, which occurs in the 75 per cent

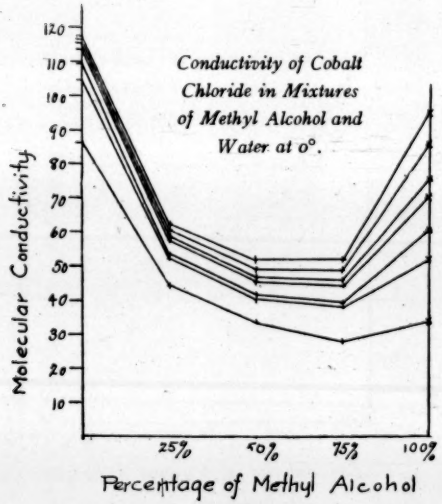


Fig. XIII.

mixture at both temperatures, is more marked at 25° than at 0°. In the case of lithium bromide, in mixtures of methyl alcohol and water, the minimum appeared more pronounced at the lower temperature. Between the 75 per cent mixture and

pure methyl alcohol the curves diverge rapidly from each other. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

The temperature coefficients increase with the dilution,

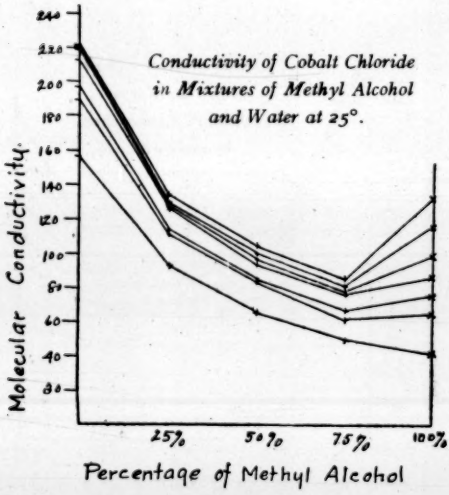


Fig. XIV.

especially in the water and pure methyl alcohol solutions. The temperature coefficients are greater in the mixtures than in the pure solvents, reaching a maximum in the 25 per cent mixture.

Table XLIX.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	30.53	73.68	0.0565
50	33.74	85.65	0.0615
100	34.64	87.60	0.0611
200	35.64	94.42	0.0660
400	37.63	97.64	0.0638
800	41.89	101.33	0.0568
1600	42.42	103.86	0.0579

Table L.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	18.17	44.75	0.0585
50	21.55	55.21	0.0625
100	22.46	57.41	0.0622
200	23.83	63.42	0.0664
400	24.76	64.00	0.0634
800	26.46	69.34	0.0648
1600	28.68	70.51	0.0583

Table LI.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	15.21	30.39	0.0399
50	19.85	41.12	0.0428
100	21.34	44.72	0.0438
200	24.02	51.70	0.0461
400	25.67	54.45	0.0448
800	27.74	59.56	0.0459
1600	29.61	63.87	0.0463

Table LII.—Conductivity of Cobalt Chloride in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	6.06	7.64	0.0104
50	10.59	13.75	0.0119
100	12.79	17.33	0.0142
200	15.43	20.93	0.0142
400	17.66	24.18	0.0148
800	20.70	28.45	0.0150
1600	23.99	33.59	0.0160

Table LIII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	86.42	30.53	18.17	15.21	6.06
50	104.31	33.74	21.55	19.85	10.59
100	109.27	34.64	22.46	21.34	12.79
200	113.73	35.64	23.83	24.02	15.43
400	115.87	37.63	24.76	25.67	17.66
800	116.71	41.89	26.46	27.74	20.70
1600	117.40	42.42	28.68	29.61	23.99

Table LIV.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	156.36	73.68	44.75	30.39	7.64
50	189.27	85.65	55.21	41.12	13.75
100	197.41	87.60	57.41	44.72	17.33
200	213.40	94.42	63.42	51.70	20.93
400	219.63	97.64	64.00	54.45	24.18
800	220.40	101.33	69.34	59.56	28.45
1600	221.50	103.86	70.51	63.87	33.59

Table LV.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Ethyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0324	0.0565	0.0585	0.0399	0.0104
50	0.0326	0.0615	0.0625	0.0428	0.0119
100	0.0322	0.0611	0.0622	0.0438	0.0142
200	0.0350	0.0660	0.0664	0.0461	0.0142
400	0.0358	0.0638	0.0634	0.0448	0.0148
800	0.0354	0.0568	0.0648	0.0459	0.0150
1600	0.0355	0.0579	0.0583	0.0463	0.0160

Tables XLIX. to LV. (Figs. XV. and XVI.) for cobalt chloride, in mixtures of ethyl alcohol and water, show a point

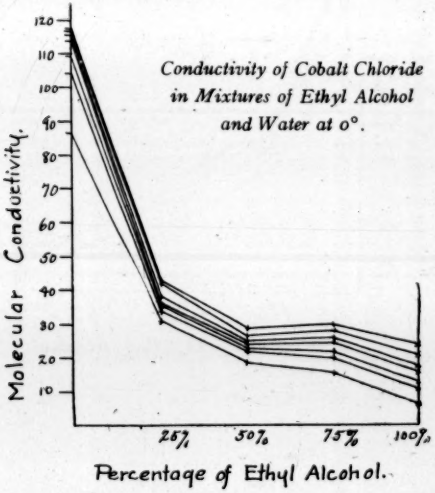


Fig. XV.

of inflection. At 0° the inflection of the curves exists at all dilutions, while at 25° the inflection is marked only at the high

dilutions. Jones and Bingham obtained curves showing points of inflection while working with calcium nitrate, in mixtures of acetone and water.

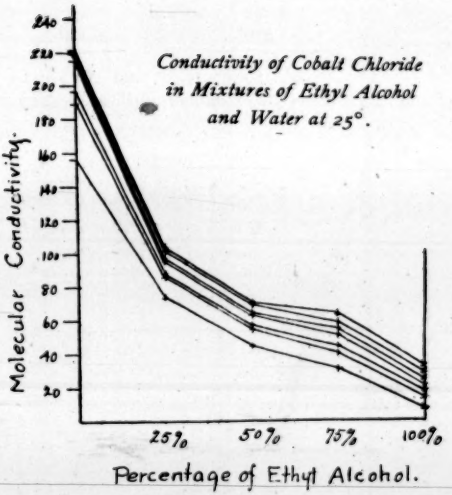


Fig. XVI.

In the pure ethyl alcohol, the temperature coefficients increase with the dilution. They are largest, for the most part, in the 50 per cent mixture.

Table LVI.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	8.82	10.76	0.00880
50	14.66	17.61	0.00805
100	17.32	21.75	0.01022
200	20.23	26.58	0.01255
400	23.75	30.08	0.01070
800	28.34	35.23	0.00972
1600	32.23	41.14	0.01106

Table LVII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	12.89	16.89	0.0124
50	21.46	27.38	0.0110
100	24.31	30.39	0.0100
200	28.63	35.89	0.0101
400	32.28	41.80	0.0118
800	39.21	48.22	0.0092
1600	46.28	58.73	0.0108

Table LVIII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Methyl Alcohol and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
10	22.49	25.53	0.00541
50	35.33	44.31	0.01020
100	40.79	49.90	0.00893
200	48.55	60.62	0.00994
400	54.78	69.42	0.01070
800	63.06	81.13	0.01150
1600	69.29	95.07	0.01490

Table LIX.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	6.06	8.82	12.89	22.49	33.46
50	10.59	14.66	21.46	35.33	51.76
100	12.79	17.32	24.31	40.79	60.89
200	15.43	20.23	28.63	48.55	70.45
400	17.66	23.75	32.28	54.78	75.64
800	20.70	28.34	39.21	63.06	86.57
1600	23.99	32.23	46.28	69.29	95.54

Table LX.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Methyl Alcohol and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	7.64	10.76	16.89	25.53	41.78
50	13.75	17.61	27.38	44.31	65.22
100	17.33	21.75	30.39	49.90	76.08
200	20.93	26.58	35.89	60.62	87.37
400	24.18	30.08	41.80	69.42	99.96
800	28.45	35.23	48.22	81.13	117.18
1600	33.59	41.14	58.73	95.07	133.33

Table LXI.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Methyl Alcohol and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0104	0.00880	0.0124	0.00541	0.00995
50	0.0119	0.00805	0.0110	0.01020	0.01040
100	0.0142	0.01023	0.0100	0.00893	0.00998
200	0.0142	0.01255	0.0101	0.00994	0.00961
400	0.0148	0.01070	0.0118	0.01070	0.01280
800	0.0150	0.00972	0.0092	0.01150	0.01410
1600	0.0160	0.01106	0.0108	0.01490	0.01580

Tables LVI. to LXI. (Figs. XVII. and XVIII.) make it clear that in a mixture of methyl and ethyl alcohols the con-

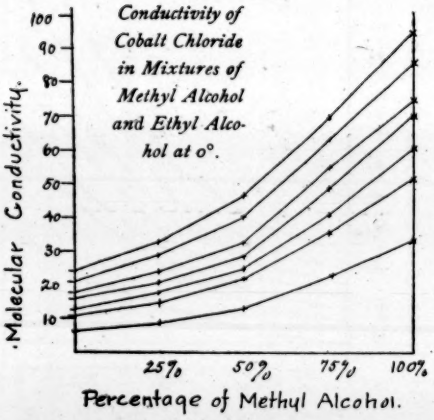


Fig. XVII.

ductivity of cobalt chloride exhibits no minimum value. There is a sagging of the curves, which shows that the values ob-

tained are less than what we should expect from the law of averages.

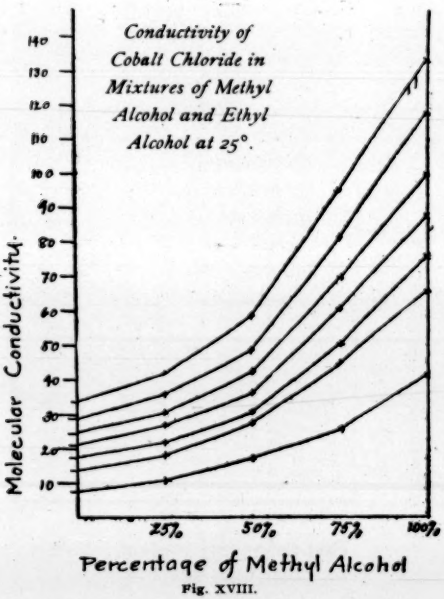


Fig. XVIII.

Table LXII.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	64.40	115.38	0.0316
200	67.88	118.42	0.0298
400	69.13	122.39	0.0308
800	72.93	126.88	0.0296
1600	79.34	134.69	0.0279

Table LXIII.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	54.42	96.89	0.0312
200	57.79	106.88	0.0340
400	60.29	112.70	0.0348
800	64.54	117.97	0.0331
1600	67.80	125.54	0.0341

Table LXIV.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	33.14	70.57	0.0452
200	37.98	84.48	0.0490
400	53.41	94.84	0.0310
800	61.16	109.76	0.0318
1600	68.51	124.95	0.0329

Table LXV.—Conductivity of Cobalt Chloride in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	10.18	9.47	—0.00279
200	10.96	9.70	—0.00460
400	11.63	9.94	—0.00581
800	12.66	10.11	—0.00806
1600	12.79	10.45	—0.00732

Table LXVI.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	109.27	64.40	54.42	33.14	10.18
200	113.73	67.88	57.79	37.98	10.96
400	115.87	69.13	60.29	53.41	11.63
800	116.71	72.93	64.54	61.16	12.66
1600	117.40	79.34	67.80	68.51	12.79

Table LXVII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	197.41	115.38	96.89	70.57	9.47
200	213.40	118.42	106.88	84.48	9.70
400	219.63	122.39	112.70	94.84	9.94
800	220.04	126.88	117.97	109.76	10.11
1600	221.50	134.69	125.54	124.95	10.45

Table LXVIII.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	0.0322	0.0316	0.0312	0.0452	—0.00279
200	0.0350	0.0298	0.0340	0.0490	—0.00460
400	0.0358	0.0308	0.0348	0.0310	—0.00581
800	0.0354	0.0296	0.0331	0.0318	—0.00806
1600	0.0355	0.0279	0.0341	0.0329	—0.00732

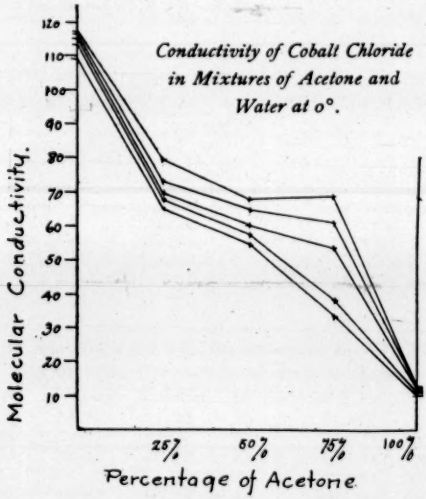


Fig. XIX.

Tables LXII. to LXVIII. (Figs. XIX. and XX.) for cobalt chloride, in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. Attention should be called to the fact that the *conductivity values in pure*

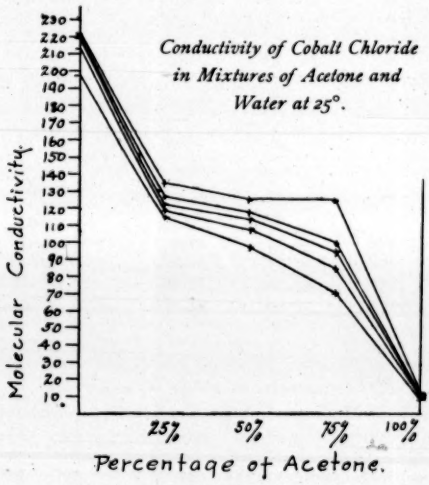


Fig. XX.

acetone, at 25°, are less than the corresponding values at 0°, thus giving negative temperature coefficients. The values in pure acetone for μ_v are small at both temperatures and at all dilutions.

Table LXIX.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	48.10	56.28	0.00680
200	57.33	64.87	0.00526
400	64.43	73.04	0.00534
800	74.60	84.46	0.00529
1600	91.57	100.09	0.00372

Table LXX.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Aretone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	35.31	39.20	0.00441
200	42.12	46.94	0.00458
400	49.39	55.47	0.00492
800	56.97	66.85	0.00694
1600	67.55	74.11	0.00388

Table LXXI.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	23.85	24.83	+0.00164
200	28.72	28.67	—0.00007
400	32.74	31.85	—0.00108
800	42.05	38.69	—0.00319
1600	50.94	47.20	—0.00294

Table LXXII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	60.89	48.10	35.31	23.85	10.18
200	70.45	57.33	42.12	28.72	10.96
400	75.64	64.43	49.39	32.74	11.63
800	86.57	74.60	56.97	42.05	12.66
1600	95.54	91.57	67.55	50.94	12.79

Table LXXIII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	76.08	56.28	39.20	24.83	9.47
200	87.37	64.87	46.94	28.67	9.70
400	99.96	73.04	55.47	31.85	9.94
800	117.18	84.46	66.85	38.69	10.11
1600	133.33	100.09	74.11	47.20	10.45

Table LXXIV.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	0.00998	0.00680	0.00441	+0.00164	—0.00279
200	0.00961	0.00526	0.00458	—0.00007	—0.00460
400	0.01280	0.00534	0.00492	—0.00108	—0.00581
800	0.01410	0.00529	0.00694	—0.00319	—0.00806
1600	0.01580	0.00372	0.00388	—0.00294	—0.00732

From a study of Tables LXIX. to LXXIV. (Figs. XXI. and XXII.), we see that cobalt chloride, in mixtures of acetone and methyl alcohol, gives neither a minimum nor a maximum

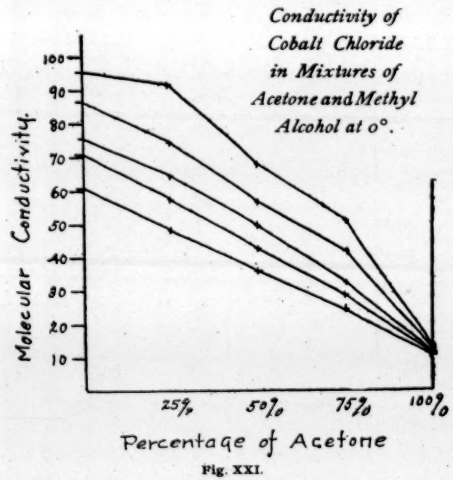


Fig. XXI.

in conductivity. The values at most of the dilutions, are what we should expect from the law of averages. It should be recalled that lithium bromide, in mixtures of acetone and

methyl alcohol, gives a maximum in conductivity at both temperatures.

By studying the temperature coefficients we see that we have to deal with a peculiar phenomenon. In the pure acetone, as already stated, we have *negative temperature coefficients*. In

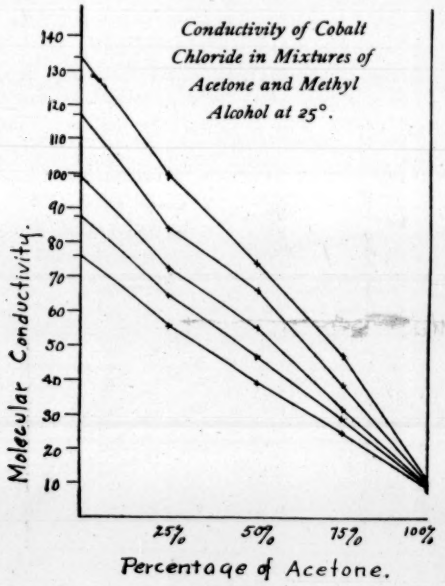


Fig. XXII.

the 75 per cent mixture of acetone and methyl alcohol, beginning with $v = 400$, we again have *negative temperature coefficients*. For $v = 100$ we have the temperature coefficient *positive*, while at $v = 200$ we have practically *no temperature coefficient of conductivity*.

Table LXXV.—Conductivity of Cobalt Chloride in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	14.40	15.43	0.00286
200	18.05	19.47	0.00314
400	21.19	23.67	0.00562
800	26.10	30.20	0.00628
1600	31.80	36.41	0.00580

Table LXXVI.—Conductivity of Cobalt Chloride in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	12.78	12.41	—0.00116
200	15.20	13.91	—0.00339
400	17.95	15.78	—0.00483
800	22.47	18.76	—0.00650
1600	28.67	23.47	—0.00726

Table LXXVII.—Conductivity of Cobalt Chloride in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
100	13.46	11.95	—0.00449
200	14.41	12.49	—0.00533
400	14.69	12.69	—0.00544
800	15.74	13.48	—0.00574
1600	17.28	14.19	—0.00715

Table LXXVIII.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	12.79	14.40	12.78	13.46	10.18
200	15.43	18.05	15.20	14.41	10.96
400	17.66	21.19	17.95	14.69	11.63
800	20.70	26.10	22.47	15.74	12.66
1600	23.99	31.80	28.67	17.28	12.79

Table LXXIX.—Comparison of the Conductivities of Cobalt Chloride in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	17.33	15.43	12.41	11.95	9.47
200	20.93	19.47	13.91	12.49	9.70
400	24.18	23.67	15.78	12.69	9.94
800	28.45	30.20	18.76	13.48	10.11
1600	33.59	36.41	23.47	14.19	10.45

Table LXXX.—Comparison of the Temperature Coefficients of Conductivity of Cobalt Chloride in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
100	0.0142	0.00286	—0.00116	—0.00449	—0.00279
200	0.0142	0.00314	—0.00339	—0.00533	—0.00460
400	0.0148	0.00562	—0.00483	—0.00544	—0.00581
800	0.0150	0.00628	—0.00660	—0.00574	—0.00806
1600	0.0160	0.00580	—0.00726	—0.00715	—0.00732

Tables LXXV. to LXXX. (Figs. XXIII. and XXIV.) for

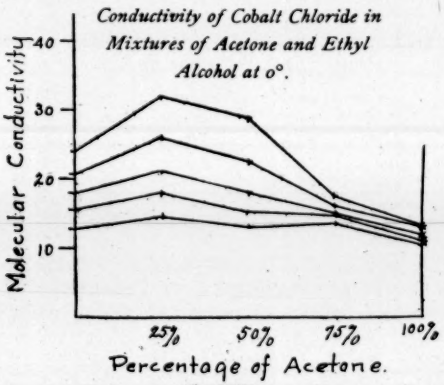


Fig. XXIII.

cobalt chloride, in mixtures of acetone and ethyl alcohol, give

a maximum in conductivity in the 25 per cent mixture, especially at high dilutions.

In the mixtures of acetone and ethyl alcohol we have *negative temperature coefficients* not only in the pure acetone and 75 per cent mixture, but also in the 50 per cent mixture. In

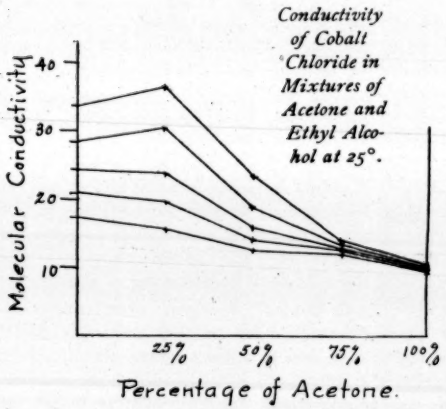


Fig. XXIV.

the case of acetone and methyl alcohol, the temperature coefficients were *negative* only in the pure acetone and 75 per cent mixture. With increase of dilution we have an increase in value of the temperature coefficients, not only in the pure solvents but also in the mixtures.

Viscosity Measurements.

It can be shown that the rate, $\frac{dx}{dt}$, at which the angular dis-

tortion of a portion of fluid changes, is proportional to the shearing stress upon the portion of the fluid. This ratio, shearing stress (S) divided by $\frac{dx}{dt}$, for a given fluid, is called its coefficient of viscosity. It may be written thus,

$$\eta = \frac{S}{\frac{dx}{dt}},$$

in which η is the coefficient of viscosity.

The viscosity of fluids is often determined by the method of Poisseule and of Hagenbach. The viscosity is calculated by the formula[1]

$$\mu = \frac{P \pi r^4 t}{8 v l},$$

where P is the actual pressure, diminished by that pressure which would be necessary to give to the fluid, while flowing through capillary tubes, the kinetic energy possessed by it ; t is the time of flow through the capillary tube of radius r and length l ; v is the volume of fluid flowing in time t.

The viscosity of fluids is, however, most commonly found by the method recommended by Ostwald.[2] We find by this method the time of flow of a fixed volume through a capillary tube, under the pressure due to the difference in level of the free surfaces of the fluid. The viscosity is found from the ratio of the time of flow for the fluid in question to the time of flow for an equal volume of water, multiplied by the specific gravity of the solution. This is expressed by the formula

$$\eta = \eta_0 \frac{S t}{S_0 t_0},$$

in which η_0 is the coefficient of viscosity for water, S_0 its specific gravity, and t_0 its time of flow, at a given temperature. The specific gravity and time of flow of the liquid in question are given by S and t, respectively.

In the following tables containing viscosity data, the values

[1] Hagenbach : Pogg. Ann., 19, 385 (1860).

[2] Ostwald-Luther : Physiko-Chemische Messungen, Zweite Aufl., p. 259.

for pure water, at 0° and 25°, taken from the work of Thorpe and Rodger,[1] are used, and all the other values are referred to them ; η is the viscosity, while ϕ, which represents fluidity, is obtained from the expression

$$\phi = \frac{1}{\eta}.$$

The density of the liquid in question, at 0° and 25°, was compared with the density of water at 0° and 25°, respectively. The density of water at 0° and 25° was taken from data given in Landolt and Börnstein's tables.

The values of η and ϕ for the solvents methyl alcohol, ethyl alcohol, acetone and mixtures of these are taken from the work of Jones and Bingham.[2]

Table LXXXI.—Fluidity of Water at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficient.
Solvent	0.01778	56.24	0.00891	112.3	0.0398

Table LXXXII.—Fluidity of Lithium Bromide in Water at 0° and 25°.

v.	μ 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.01874	53.36	0.009077	110.17	0.0425
1600	0.01827	54.73	0.008963	111 57	0.0415
Solvent	0.01778	56.24	0.008910	112.30	0.0398

Table LXXXIII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.034216	29.22	0.01440	69.43	0.0550
1600			0.01420	70.42	
Solvent	0.03335	29.98	0.01409	70.94	0.0546

[1] Phil. Trans., 185A, 307 (1894).
[2] This Journal, 34, 481 (1905).

Table LXXXIV.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.03703	27.00	0.01680	59.53	0.0482
1600			0.01639	61.01	
Solvent	0.03642	27.46	0.01611	62.04	0.0503

Table LXXXV.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Methyl Alcohol and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10			0.01345	74.32	
1600			0.01298	77.00	
Solvent	0.02576	38.82	0.01283	77.92	0.0402

Table LXXXVI.—Fluidity of Lithium Bromide in Methyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.008994	111.18	0.006124	163.28	0.0187
1600	0.008346	119.82	0.005635	177.46	0.0192
Solvent	0.008185	122.20	0.005659	176.70	0.0178

Table LXXXVII.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Methyl Alcohol and Water at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	53.36	29.22	27.00		111.18
1600	54.73				119.82
Solvent	56.24	29.98	27.46	38.82	122.20

Fluidities at 25°.

10	110.17	69.43	59.53	74.32	163.28
1600	111.57	70.42	61.01	77.00	177.46
Solvent	112.30	70.94	62.04	77.92	176.70

Table LXXXVIII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Methyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0425	0.0550	0.0482		0.0187
1600	0.0415				0.0192
Solvent	0.0398	0.0546	0.0503	0.0402	0.0178

Table LXXXIX.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10			0.01832	54.57	
1600			0.01818	55.00	
Solvent	0.05264	18.99	0.01810	55.22	0.0763

Table XC.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ 0°.	ϕ 0°.	η 25°.	ϕ 25°.	Temperature coefficients.
10	0.06922	14.45	0.02453	40.77	0.0728
1600			0.02407	41.53	
Solvent	0.06720	14.88	0.02405	41.56	0.0717

Table XCI.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Ethyl Alcohol and Water at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.02204	45.36	
1600			0.02139	46.75	
Solvent	0.05167	19.35	0.02118	47.21	0.0575

Table XCII.—Fluidity of Lithium Bromide in Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.02441	40.96	0.01366	73.18	0.0314
1600	0.02199	45.48	0.01224	81.69	0.0318
Solvent	0.01856	53.88	0.01106	90.35	0.0271

Table XCIII.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Ethyl Alcohol and Water at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	53.36		14.45		40.96
1600	54.73				45.48
Solvent	56.24	18.99	14.88	19.35	53.88

Fluidities at 25°.

10	110.17	54.57	40.77	45.36	73.18
1600	111.57	55.00	41.53	46.75	81.69
Solvent	112.30	55.22	41.56	47.21	90.35

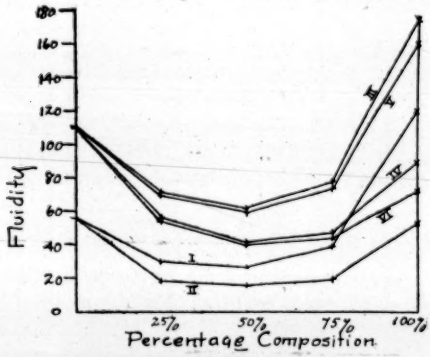
Table XCIV.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Ethyl Alcohol and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0425		0.0728		0.0314
1600	0.0415				0.0318
Solvent	0.0398	0.0763	0.0717	0.0575	0.0271

Tables LXXXI. to XCIV. (Fig. XXV.) show that there is a minimum of fluidity not only in the case of the mixtures of the pure solvents—methyl alcohol and water, and ethyl alcohol and water—at both temperatures, but also in the case of lithium bromide dissolved in the above solvents. The fluidity of a liquid being the reciprocal of its viscosity, the viscosity curve would pass through a maximum in the above cases. A large number of investigations have been carried out on the viscosities of the alcohols and water, notably, by Poisseuille,[1] Stephan,[2] Pagliani and Battelli,[3] Noack,[4] and Traube.[5] Quite recently some work has been done on the viscosity of mixtures

[1] Mem. Inst. Paris, 9, 433 (1896).
[2] Wied. Ann., 17, 673 (1883).
[3] Atti. di R. Ac. delle Sc. d. Torino, 20, 607 (1885).
[4] Wied. Ann., 27, 289 (1886).
[5] Ber. d. chem. Ges., 19, 871 (1886).

of the alcohols and water by Dunstan,[1] Blanchard,[2] and Varenne and Godefroy.[3] All of these workers have found that, in the



I. Methyl Alcohol and Water at 0°.
II. Ethyl Alcohol and Water at 0°.
III. Methyl Alcohol and Water at 25°.
IV. Ethyl Alcohol and Water at 25°.
V. 0.1 N LiBr in CH_3OH and H_2O at 25°.
VI. 0.1 N LiBr in C_2H_5OH and H_2O at 25°.

Fig. XXV.

case of mixtures of the alcohols and water, the viscosity of the mixture is much greater than would be expected from the law of averages.

Jones and Carroll[4] have calculated the various fluidities of mixtures of methyl and ethyl alcohol and water, for the temperatures 0°, 10°, 20° and 30°, from the results of Pagliani and Battelli[4] and of Traube[4] and have plotted the fluidity curves. Their curves were similar to those which we obtained.

[1] J. Chem. Soc., **85**, 817 (1904).
[2] J. Am. Chem. Soc., **26**, 1315 (1904).
[3] Compt. rend., **137**, 992 (1903); **138**, 990 (1904).
[4] *Loc. cit.*

Table XCV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Methyl Alcohol and Water.

Fluidity.

v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0398	0.0546	0.0503	0.0402	0.0178
		Conductivity.				
10	LiBr	0.0329	0.0435	0.0410	0.0314	0.01590
1600	LiBr	0.0357	0.0437	0.0420	0.0335	0.01810
10	$CoCl_2$	0.0324	0.0440	0.0400	0.0324	0.00995
1600	$CoCl_2$	0.0355	0.0472	0.0411	0.0257	0.01580

Table XCVI.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Ethyl Alcohol and Water.

Fluidity.

v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0398	0.0763	0.0717	0.0575	0.0271
		Conductivity.				
10	LiBr	0.0329	0.0557	0.0595	0.0437	0.0253
1600	LiBr	0.0357	0.0448	0.0596	0.0465	0.0242
10	$CoCl_2$	0.0324	0.0565	0.0585	0.0399	0.0104
1600	$CoCl_2$	0.0355	0.0579	0.0583	0.0463	0.0160

Tables XCV. and XCVI. show that the temperature coefficients of fluidity and conductivity vary in the same manner. The latter are, however, uniformly smaller than the former.

Table XCVII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.01366	73.19	
1600			0.01356	73.72	
Solvent	0.0293	34.12	0.01276	78.37	0.0518

Table XCVIII.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.03102	32.23	0.01428	70.00	0.0468
1600			0.01369	73.00	
Solvent	0.03027	33.03	0.01330	74.96	0.0508

Table XCIX.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.009562	104.58	
1600			0.009263	107.95	
Solvent	0.017	58.8	0.008904	112.30	0.0364

Table C.—Fluidity of Lithium Bromide in Acetone at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.004302	232.45	0.003484	286.96	0.0093
1600	0.004117	242.85	0.003339	299.42	0.0093
Solvent	0.004097	244.10	0.003237	308.90	0.0106

Table CI.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Acetone and Water at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	53.36		32.23		232.45
1600	54.73				242.85
Solvent	56.24	34.12	33.03	58.80	244.10

Fluidities at 25°.

10	110.17	73.19	70.00	104.58	286.96
1600	111.57	73.72	73.00	107.95	299.42
Solvent	112.30	78.37	74.96	112.30	308.90

Table CII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0425		0.0468		0.0093
1600	0.0415				0.0093
Solvent	0.0398	0.0518	0.0508	0.0364	0.0106

Table CIII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.005455	183.30	
1600			0.005068	197.29	
Solvent	0.006498	153.90	0.004615	216.70	0.0163

Table CIV.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.006265	159.6(?)	0.004527	220.87	0.0153
1600	0.005774	173.17	0.004234	236.18	0.0145
Solvent	0.005336	187.40	0.003891	257.10	0.0148

Table CV.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.003775	264.88	
1600			0.003581	279.25	
Solvent	0.004501	222.20	0.003446	290.10	0.0122

Table CVI.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	111.18		159.6(?)		232.45
1600	119.82		173.17		242.85
Solvent	122.20	153.90	187.40	222.20	244.10

Fluidities at 25°.

10	163.28	183.30	220.87	264.88	286.96
6100	177.46	197.29	236.18	279.25	299.42
Solvent	176.70	216.70	257.00	290.10	308.90

Table CVII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0187		0.0153		0.0093
1600	0.0192		0.0145		0.0093
Solvent	0.0178	0.0163	0.0148	0.0122	0.0106

Table CVIII.—Fluidity of Lithium Bromide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.008218	121.69	
1600			0.007731	129.34	
Solvent	0.01041	96.08	0.006714	148.90	0.022

Table CIX.—Fluidity of Lithium Bromide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10	0.007353	136.0	0.005554	180.05	0.0129
1600			0.005165	193.59	
Solvent	0.006801	147.0	0.004874	205.20	0.0148

Table CX.—Fluidity of Lithium Bromide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ 0°.	ϕ 0°.	μ 25°.	ϕ 25°.	Temperature coefficients.
10			0.004237	235.99	
1600			0.003874	258.10	
Solvent	0.00499	200.4	0.003776	264.80	0.01296

Table CXI.—Comparison of the Fluidities of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol at 0° and 25°.

Fluidities at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	40.96		136.00		232.45
1600	45.48				242.85
Solvent	53.88	96.08	147.00	200.40	244.10

Fluidities at 25°.

10	73.18	121.69	180.05	235.99	286.96
1600	81.69	129.34	193.59	258.10	299.42
Solvent	90.35	148.90	205.20	264.80	308.90

Table CXII.—Comparison of the Temperature Coefficients of Lithium Bromide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	0.0314		0.0129		0.0093
1600	0.0318				0.0093
Solvent	0.0271	0.022	0.0148	0.01296	0.0106

Tables XCVII. to CXII. (Figs. XXVI., XXVII. and XXVIII.) show that there is a minimum of fluidity for the

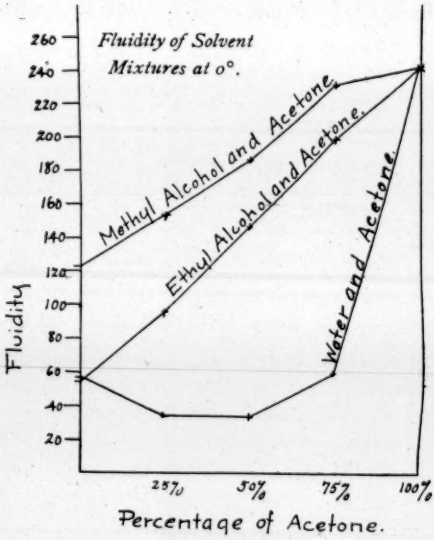


Fig. XXVI.

solvents only in the case of acetone and water. This fact was

pointed out by Jones and Bingham. Lithium bromide, in a mixture of acetone and water, shows a similar minimum. Jones and Bingham also found that in the mixtures of acetone with methyl alcohol, somewhat larger values were obtained than would be expected from the fluidities of the pure solvents.

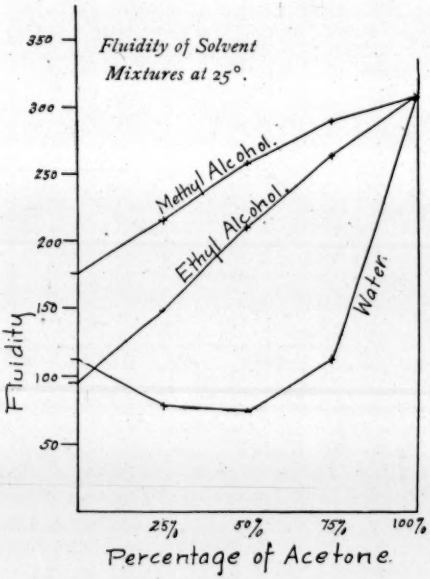


Fig. XXVII.

This effect is not quite so apparent in the case of acetone and ethyl alcohol. We obtained similar results in the case of lithium bromide in these solvents. It is to be especially noticed

that the viscosity curves in all cases, for mixtures of acetone with the alcohols, show a marked sagging.

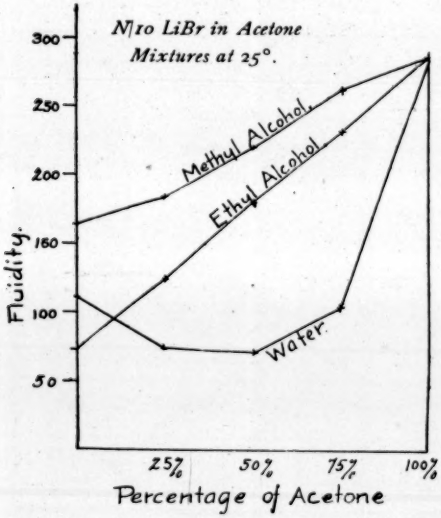


Fig. XXVIII.

Table CXIII.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Water.

v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
		Fluidity.				
Solvent		0.0398	0.0518	0.0508	0.0364	0.0106
		Conductivity.				
10	LiBr	0.0329	0.0429	0.0432	0.0315	0.00729
1600	LiBr	0.0357	9.0401	0.0437	0.0372	0.00847
100	$CoCl_2$	0.0322	0.0316	0.0312	0.0452	—0.00279
1600	$CoCl_2$	0.0355	0.0279	0.0341	0.0329	—0.00732

Table CXIV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Methyl Alcohol.

Fluidity.

v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0178	0.0163	0.0148	0.0122	0.0106

Conductivity.

10	LiBr	0.0159	0.0143	0.00939	0.0112	0.00729
1600	LiBr	0.0181	0.0153	0.01340	0.0104	0.00847
100	$CoCl_2$	0.00998	0.0068	0.00441	0.00164	—0.00279
1600	$CoCl_2$	0.0158	0.00372	0.00388	—0.00294	—0.00732

Table CXV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Ethyl Alcohol.

Fluidity.

v.	Dissolved substance.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Solvent		0.0271	0.022	0.0148	0.0129	0.0106

Conductivity.

10	LiBr	0.0253	0.0168	0.0135	0.0085	0.00729
1600	LiBr	0.0242	0.0206	0.0159	0.0103	0.00847
100	$CoCl_2$	0.0142	0.00286	—0.00116	—0.00449	—0.00279
1600	$CoCl_2$	0.0160	0.00580	—0.00726	—0.00715	—0.00732

Tables CXIII. to CXV. show that the temperature coefficients of fluidity and conductivity, in the case of lithium bromide, vary in the same manner, although the latter are, for the most part, smaller than the former. Abnormal results were obtained with cobalt chloride in mixtures of acetone with the alcohols, in so far as the temperature coefficients of conductivity are concerned.

PART III.

DISCUSSION OF RESULTS.

A. Fluidity and Conductivity.

That there is a parallelism between conductivity and fluidity has been previously pointed out in the introduction to this

paper; and since the conductivity of a solution is dependent, in part, upon its fluidity, we shall first discuss the fluidity curves and then, in connection with them, the conductivity curves.

When methyl alcohol, ethyl alcohol, or acetone is mixed with water there is a contraction in volume and an evolution of heat, and we have a large deviation of the fluidity curve from a straight line. In other words, we have a marked viscosity maximum—a fact which seems to be more or less general whenever water and organic solvents are mixed. In addition to methyl and ethyl alcohols and acetone, propyl and isopropyl alcohols, propionic acid, butyric and isobutyric acids give, when mixed with water, viscosity maxima. In every case there is a greater decrease in fluidity than would be expected from the law of averages.

When methyl and ethyl alcohol are mixed they do not exhibit the same phenomena as is shown in the case of mixtures of organic solvents with water. Arrhenius[1] states that there is no observable change when these alcohols are brought together.

When acetone is mixed with methyl or ethyl alcohol, the fluidity curve of the mixture is approximately a straight line. The same is true when we have an electrolyte dissolved in mixtures of these solvents.

From a consideration of the fluidity curves and conductivity curves for lithium bromide in mixtures of methyl alcohol and water, it is quite evident that the minimum of fluidity corresponds to the minimum of conductivity, both generally occurring in the 50 per cent mixtures of the solvents. The drop in fluidity is more pronounced at the lower temperature, and, similarly, the drop in conductivity. In fact, at the higher temperature, the minimum of conductivity occurs in the 75 per cent mixture until $v = 100$, where there is a shifting of the minimum to the 50 per cent mixture.

In the case of mixtures of ethyl alcohol and water, the minimum of fluidity is in the 50 per cent mixture, and more marked at the lower temperature. The conductivity minimum in this case occurs in the 75 per cent mixture, and is very

[1] Z. physik. Chem., 1, 285 (1887).

slight indeed at 25°, although the values, in each case, are much less than we should expect from the law of averages. Thus we have, in both the case of methyl alcohol and water, and of ethyl alcohol and water, a tendency for the shifting of the minimum towards the mixture containing the greater per cent of alcohol, whenever we have a rise in temperature.

Stephan,[1] working with mixtures of ethyl alcohol and water, found that the temperature coefficients of conductivity and of fluidity were very similar. A minimum in his curves was observed, and he proposed the relations

$$k = \frac{K H}{\eta} \quad \text{and} \quad k = \frac{w K H}{w' \eta},$$

the first holding for the mixtures up to the minimum point, and the second from that point on. K is the same in both formulæ, and is the conductivity of the equivalent aqueous solution of the electrolyte; k is the conductivity in the mixture; H and η are the viscosity coefficients for water and for the mixture, respectively. w and w' are the per cents of water in the mixture and in the aqueous alcoholic mixtures of minimal fluidity, respectively. Stephan concluded that each ion carries with it molecules of the solvent, and that the ionic friction consists in friction between these molecules and the rest of the solvent. Thus we have very early the idea of ionic hydration introduced.

This idea of ionic hydration, or ionic spheres, was further extended by Kohlrausch,[2] who proposed the hypothesis that "about every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion . . . . . The electrolytic resistance is a frictional one that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portions of the solvent diminishes as the atmosphere becomes of greater dimensions. For a slow moving ion there would be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, providing the atmosphere

[1] Wied. Ann., 17, 673 (1883).
[2] P. Roy. Acad., 71, 338 (1903).

does not change its dimensions with temperature. However, if the atmosphere becomes smaller with rise in temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. This seems to be true for the slowest moving, univalent ion, Li."

In the case of the alcohols and water, this minimum of conductivity is entirely accounted for by some investigators on the basis of the formation of hydrates. This view was suggested by Zelinsky and Krapiwin.[1] The minimum in fluidity is attributed to the formation of molecular aggregations, which are formed by mixing the solvents. In the case of methyl alcohol and acetone, or ethyl alcohol and acetone, since the fluidity curve is a straight line, we conclude that the molecular aggregations of these solvents are not changed in size when the solvents are mixed. This is what we should expect if the fluidities are additive, a fact which has been shown recently by Bingham[2] to be true. From the above, we see that the conductivity minimum is generally accompanied by a fluidity minimum, and that both minima are more marked at the lower temperatures. Also, that an increase in temperature tends to shift the minimum towards the mixture containing a greater per cent of alcohol or acetone, as the case may be. Thus, we believe that *a diminution in the fluidity of the solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor in causing the minimum of conductivity.* In the case when the conductivity minimum is in the 75 per cent mixture, while the minimum of fluidity is in the 50 per cent mixture, as it is with ethyl alcohol and water, we believe that the explanation is to be found in the fact that the ethyl alcohol and water mixtures have a much greater viscosity than those of methyl alcohol and water. When the minimum shifts with an increase in dilution, there may be an increase in dissociation.

However, we do not believe that the above explanation accounts entirely for the conductivity minimum. Since conductivity is dependent upon the number and velocity of the ions,

[1] Z. physik. Chem., 21, 35 (1896).
[2] THIS JOURNAL, 35, 195 (1906).

there is no doubt but that an increase in viscosity retards the velocity of the ions, but we think that *the change in the size of the ionic sphere, or the atmosphere which surrounds the ion,* should be taken into account. The movement of the ion depends not only upon its composition, but also upon its attraction for the surrounding solvent, which causes an atmosphere of the solvent to be formed about the ion. Lithium is an extremely slow moving ion, or, in other words, one with a very large ionic sphere. Now the atmosphere becomes larger with decreasing temperature. Thus, we have evidence that the change in dimensions of the ionic spheres must be taken into account in dealing with fluidity and, consequently, with conductivity from the fluidity data of lithium bromide. The fluidity values are, on the whole, small, due to the large atmosphere surrounding the lithium ion. This atmosphere increases with decrease in temperature, and thus produces the smaller fluidity values at the lower temperature.

We should not, however, lose sight of the fact that if viscosity is in any way dependent upon the attractions between the molecules, whenever there is a contraction in mixing two solvents as there is in the case of the alcohols and water, then the molecules will be brought closer together and the attractions will be increased between the molecules. It is obvious from this that we should get a fluidity value different from that calculated from the law of averages.

The statement was made above that fluidities are sometimes additive. That is, the resulting fluidity of a mixture of two solvents is equivalent to the sum of the fluidities of each solvent. Formulated, this would be,

$$(k_1 + k_2)\phi = k_1\phi_1 + k_2\phi_2 \ldots\ldots (1),$$

where ϕ is the resultant fluidity, ϕ_1 and ϕ_2 the respective fluidities of the components of amounts k_1 and k_2.

Jones and Bingham[1] have pointed out that this expression is similar to the conception which we have in electricity, where the conductance of several conductors, in parallel, is represented by the sum of their separate conductances. The con-

[1] THIS JOURNAL, 34, 481 (1905).

ductance of a pair of conductors, of different material, is, for a unit length,

$$(\sigma_1 + \sigma_2)C = c_1\sigma_1 + c_2\sigma_2,$$

where σ_1 and σ_2 are the areas of cross section of the conductors, c_1 and c_2 their respective conductances, and C the resulting conductance.

By a simple mathematical deduction, Jones and Bingham have shown that if fluidities are additive, viscosities cannot be additive. They derived the formula

$$K'_1 H = \frac{\eta_1 \eta_2}{\mu_2 - \eta_1} \quad \ldots\ldots\ldots\ldots (2),$$

where η_1 and μ_2 are the viscosities of the components and H that of the mixture

$$K'_1 = K_1 + \frac{\eta_1}{\eta_2 - \eta_1},$$

where K_1 has the same significance as in equation 1.

Since $\frac{\eta_1 \eta_2}{\eta_2 - \eta_1}$ is a constant, equation (2) is considered to represent an equilateral hyperbola, the Y-axis of which is at a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin to which equation (1) is referred. Thus, the conclusion is drawn that the *hyperbola is the normal curve for viscosities and not the straight line.* This fact accounts for the sagging of the viscosity curves or, in other words, the viscosities of the mixtures are not proportional directly to the amounts of the components. The above only holds in case we have a mixture of two liquids which are made up of particles that do not interact in any way with each other, as in the case of acetone and ethyl alcohol.

When we have contraction or expansion on mixing two liquids, the hyperbola would not represent the viscosity curve of the mixtures, but we get a curve of the form already described.

By examining the viscosity data of the mixtures of acetone with methyl alcohol and ethyl alcohol, and also the data for lithium bromide in these mixtures, we see that the viscosity of

a mixture is, in most instances, slightly lower than would be expected from the law of averages. In these cases the fluidity curves are straight lines. In the recent work of Bingham[1] this has been shown to be frequently true where organic solvents are mixed.

Let us now consider the maximum in conductivity obtained with lithium bromide in mixtures of acetone with methyl and ethyl alcohols. Cobalt chloride gave a maximum in conductivity only in the case of acetone with ethyl alcohol. In the former case the maximum occurs entirely in the 75 per cent mixture, while in the latter only in the 25 per cent mixture.

This phenomenon had also been observed by Jones and Bingham, working with lithium nitrate and calcium nitrate in mixtures of acetone with the alcohols. As pointed out by them, this must be due either to an increase in dissociation in the 75 per cent mixture, or to the diminution in the size of the ionic spheres.

In discussing the fluidity curves, we pointed out that, when acetone was mixed with the alcohols, we did not obtain complex molecular aggregates. It is, then, impossible for the mixture to be more associated than the pure solvents, and we, therefore, cannot have an increase in dissociation if the hypothesis of Dutoit and Aston is true.

From an examination of the conductivity tables of lithium bromide we see that we have by no means reached the limiting conductivity values in the pure acetone, or the 75 per cent mixtures of acetone with the alcohols. It is nearly reached only with the pure alcohols. Thus, we could not have complete dissociation in these mixtures. The conductivity maximum should also manifest itself in the case of cobalt chloride, in mixtures of acetone with methyl alcohol, but this is contrary to what we have observed. We, therefore, accept the view, held tentatively by Jones and Bingham, that *the maximum in conductivity is due primarily to a change in the dimensions of the ionic spheres.*

Attention should be called to the fact that cobalt chloride, in mixtures of acetone with water, shows a tendency toward a

[1] *Loc. cit.*

maximum in conductivity in the 75 per cent mixture, notwithstanding the great decrease in fluidity.

Thus we see that the tendency towards a maximum in conductivity, in mixtures of acetone with other solvents, is very marked.

Let us now sum up the cases where maxima in conductivity have been obtained in the acetone mixtures. Jones and Bingham obtained the maximum with lithium nitrate and calcium nitrate, in mixtures of acetone with methyl or ethyl alcohol. Under similar conditions, we have obtained the maximum in the case of lithium bromide in these mixtures. Cobalt chloride gave the maximum only in a mixture of acetone with ethyl alcohol. Jones and Bingham showed that lithium nitrate and calcium nitrate, in mixtures of acetone with water, show a tendency towards a maximum. We have observed the same fact with cobalt chloride in a mixture of acetone with water.

B. Temperature Coefficients.

That conductivity is affected by temperature was observed as early as 1844 by Ohm.[1] In 1875 it was established by Kohlrausch[2] that the conductivity of aqueous solutions of electrolytes, in general, increases with the temperature and that, for ordinary temperatures, this relation may be represented by the linear equation,

$$\lambda_t = \lambda_0 (1 + \alpha t),$$

where λ represents the molecular conductivity, t the temperature in question, and α is a constant.

Arrhenius,[3] in 1889, showed, from theoretical considerations, that the relation between conductivity and temperature is not a linear one, as suggested by Kohlrausch. He established the fact that conductivity at first increases with rise in temperature, reaches a maximum value, and then decreases. He verified this for solutions of hypophosphorous acid and phosphoric acid, the former having a maximum conductivity at about 55° and the latter at 75°.

[1] Pogg. Ann., 63, 403 (1844).
[2] *Ibid.*, 154, 224 (1875).
[3] Z. physik. Chem., 4, 96 (1889).

Since Arrhenius made these measurements, maxima of conductivity have been found for solutions of copper sulphate and for a number of organic acids. The maximum conductivity of most aqueous solutions, however, is at so high a temperature that experimental difficulties have prevented the verification of the above theory of Arrhenius for many electrolytes.

Maxima of conductivity have been found by Miss Maltby,[1] Hagenbach,[2] Noyes and Coolidge,[3] and others, all working at elevated temperatures.

In the case of non-aqueous solvents there is more evidence available for the existence of conductivity-temperature curves, containing maxima.

Franklin and Kraus[4] found that, at high temperatures, the conductivity of solutions in liquid ammonia decreases with rise in temperature. Miss Maltby[5] showed that, at atmospheric temperatures, the conductivity of an ethereal solution of hydrochloric acid decreases as the temperature rises. Cattaneo[6] obtained negative temperature coefficients in ether and alcohol.

Kraus,[7] in his investigations of solutions in methyl and ethyl alcohols, also found that the conductivity passes through a maximum with rise in temperature.

Jones[8] explains these maxima in the conductivity curves thus: "The ions move faster and faster with rise in temperature, increasing the conductivity. The association of the solvent becomes less and less with rise in temperature and, consequently, its dissociating power becomes less and less. This, of course, diminishes the conductivity. The maximum in the conductivity curve represents the temperature at which *these opposite influences become equal.*"

In a very recent article, Jones and West[9] have pointed out the effect of temperature on dissociation, and have worked out

[1] Z. physik. Chem., **18**, 155 (1895).
[2] Ann. d. Phys., **8**, 276 (1901).
[3] Z. physik. Chem., **46**, 323 (1904). J. Am. Chem. Soc., **26**, 134 (1904).
[4] THIS JOURNAL, **24**, 83 (1900).
[5] Z. physik. Chem., **18**, 133 (1895).
[6] Rend. Lincei, [5], **2**, 1, 295 (1893); [5], **2**, 2, 112 (1893).
[7] Phys. Rev., **18**, 40 (1904).
[8] THIS JOURNAL, **31**, 584 (1904).
[9] *Ibid.*, **34**, 357 (1905).

a large number of temperature coefficients of conductivity in aqueous solutions. They employed 32 substances, inorganic and organic, with very different degrees of dissociation. The range of temperature over which their investigation extended was from 0° to 35°. They found that, while conductivity increases with rise in temperature, dissociation decreases with rise in temperature.

Jones[1] has recently pointed out the bearing of hydrates on the temperature coefficients of conductivity of aqueous solutions. Jones and West, in their work, showed that with an increase of temperature there was a decrease in dissociation. Therefore, *the increase in conductivity with rise in temperature is primarily due to an increase in the velocities with which the ions move.* The velocity of the ions is conditioned chiefly by the viscosity of the medium and the size of the ion. At the higher temperature the force which drives the ion is greater, and the fluidity of the medium through which the ion moves would be greater. Both of these factors increase the velocity of the ions and, consequently, increase the conductivity as the temperature is raised. Jones calls attention to the fact that the *mass of the ion decreases with rise in temperature.* He does not refer to the charged atom or group of atoms which are usually termed the ion, but to this charged nucleus plus a larger or smaller number of molecules of water, which are attached to it and which it drags along with it in its motion through the remainder of the solvent.

At the higher temperature the hydrate formed by the ion is less complex than at a lower temperature. The less the number of molecules of water combined with the ion, the smaller the mass of the ion and the less its resistance when moving through the solvent. Therefore, the ion will move faster at the higher temperature and the conductivity of the solution will increase with rise in temperature.

Jones also points out the fact that, at the higher dilution, the temperature coefficient of conductivity for any given substance is greater than at the lower dilutions. The hydrate at the higher dilution is more complex than at the lower. This

[1] THIS JOURNAL, 38, 445 (1906).

being so, the change in the composition of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity is greater the more dilute the solution.

After this brief review of the most important facts which have been found concerning the effect of temperature on conductivity, let us study the temperature coefficients which we obtained.

In a previous paper[1] we have pointed out the presence of *solvates* in non-aqueous solutions, not only in the case of lithium bromide but also for several other electrolytes. That there is a combination of the solvent with the dissolved substance to form *solvates* is now a generally accepted fact.

In the pure solvents, with but one exception, the temperature coefficients of conductivity are greater at the higher dilutions than at the lower. This may be explained by the fact that if the solvate at the higher dilution is more complex than at the lower, then the change in the composition of the solvate in question, with change in temperature, is greater at the higher dilution. Consequently, the more dilute the solution the greater the temperature coefficient of conductivity.

In the mixtures of the solvents we found that, in practically every case, there was an increase in the temperature coefficients with an increase in dilution. There is a combination of the solvent and dissolved substance to form a *solvate*, and we believe the explanation is the same as that given above.

This same fact has been found to be true by Jones and his co-workers in many other cases. If we examine the data obtained by Jones and Lindsay in their work, we see that the temperature coefficients of conductivity increase with the dilution for potassium iodide, ammonium bromide, strontium iodide and lithium nitrate, in mixtures of water, methyl and ethyl alcohol and binary mixtures of these solvents. In some few cases the increase, however, is small. Similar results are found by a study of the work of Jones and Carroll, who worked with a number of electrolytes in mixtures of the same

[1] THIS JOURNAL, **35**, 316 (1906).

solvents. Jones and Bingham, in their work, observed the fact that in acetone, and in some few acetone mixtures, the temperature coefficients decreased with the dilution. In most cases, however, there was a slight increase with an increase in dilution.

Thus, the fact that at the higher dilutions the temperature coefficients are greater than at the lower, holds, in general, not only for aqueous solutions, as pointed out by Jones, but also for organic solvents and for mixtures of these solvents in most of the cases thus far studied.

We have seen in the historical review that there are a few cases on record where the conductivity decreases with rise in temperature. This has been found to be true, generally, only at high temperatures and after a maximum has been reached. Bousfield and Lowry[1] have shown that we should expect this upper limit of conductivity on account of the decrease in dissociation with rise in temperature. They combine the formula of Slotte[2] for variation of fluidity,

$$\eta_0/\eta = 1 + \beta t)^n,$$

which holds at low temperatures, with that of Abegg and Seitz for decrease in dielectric constant,

$$D/D' = e^{-at},$$

and give as the complete formula, which represents the effect of temperature on conductivity,

$$\frac{K_t}{K_0} = \frac{\rho_v}{\rho_0}(1 + \beta t)^n e^{-at}.$$

At low temperatures negative temperature coefficients have been found in very few instances. As was stated before, we have found *negative* temperature coefficients in the case of cobalt chloride in acetone; in a 75 per cent mixture of acetone with methyl alcohol; also in 50 and 75 per cent mixtures of acetone with ethyl alcohol. In the 75 per cent mixture of acetone with methyl alcohol, at the dilution $v = 200$, we have practically *no temperature coefficient of conductivity*. In all

[1] P. Roy. Soc., 71, 42 (1902).
[2] Beibl., 16, 182 (1892).

cases these negative coefficients were found while working at *ordinary temperatures*.

Acetone and the alcohols are considered to be highly associated compounds at ordinary temperatures. We have shown that the diminishing dissociating power of a solvent with rise in temperature must overcome the increasing velocities of the ions, in order to have a decrease in conductivity with rise in temperature. Acetone and the alcohols are more associated at 0° than at 25° and, consequently, their dissociating power is greater at the lower temperature. The ions, however, move faster at 25° than at 0°. Since we have found negative temperature coefficients, we believe that the effect due to diminishing dissociation more than overcomes the effect due to the increasing velocities of the ions.

We think, nevertheless, that there is another factor which comes into play. We are inclined to the view that the solvates which are formed in these cases may be more stable at the higher temperature and, therefore, we should expect the reaction which gave rise to it to be endothermic. At the dilution where the temperature coefficient of conductivity is practically zero, these *opposite influences which affect conductivity become equal.* The point where we have a temperature coefficient, which is practically zero, corresponds to the maximum in conductivity obtained by other workers at high temperatures.

Summary.

1. We have measured the fluidities of water, methyl alcohol, ethyl alcohol, acetone, and binary mixtures of these solvents; also the fluidities of solutions of lithium bromide in these mixtures.

2. We have also measured the conductivity of various concentrations of lithium bromide and cobalt chloride, in the above named solvents and mixtures of these with one another.

3. The conductivities, in the case of mixtures of the alcohols with water, exhibit a minimum. The same fact was found to be true in the case of mixtures of acetone with water. This minimum in conductivity was found to be more pronounced at the lower temperature, and has been shown to be

intimately connected with the minimum in fluidity observed in the above mixtures.

4. The conductivities of lithium bromide, in mixtures of methyl and ethyl alcohols, are what we should expect from the law of averages. The conductivity curves are nearly straight lines. In the case of cobalt chloride, in these mixtures, there was a slight sagging of the curves.

5. In the case of lithium bromide, in mixtures of acetone with the alcohols, the fluidities are what we should expect from the law of averages—the fluidity curves are straight lines. The same has been found to be true in the case of the pure solvents. This indicates that acetone and the alcohols do not form more complex aggregations when mixed than when unmixed. Here again, conductivity has been shown to be connected with fluidity.

6. Lithium bromide, however, gives a pronounced maximum in conductivity, in mixtures of acetone with methyl or ethyl alcohol. The same phenomenon was observed in the case of cobalt chloride in mixtures of acetone with ethyl alcohol. We believe this maximum is due, primarily, to a diminution in the dimensions of the atmosphere about the ions.

7. We think, also, that the changes in the size of the ionic spheres should be considered as a factor in causing the conductivity minimum as well as the maximum.

8. We have determined the temperature coefficients of conductivity and fluidity, and found them to be of the same order of magnitude. Lithium bromide, in the mixtures studied, showed, with rise in temperature, a large increase in conductivity, due to increase in fluidity. The temperature coefficients of lithium bromide in the above mixtures are, therefore, all positive.

9. Cobalt chloride, however, in some of the acetone mixtures, at *ordinary temperatures*, gave *negative temperature coefficients*. We think this is due not only to the effect of the diminishing dissociation more than overcoming the effect due to the increasing velocity of the ions, but also to the fact that the solvates formed in these cases may be more stable at the higher tem-

perature. We should, therefore, expect, the reaction which gave rise to the solvates to be endothermic.

10. We have found for our substances, in a given mixture of solvents, a dilution where the temperature coefficient of conductivity is practically zero. This corresponds to the maximum in conductivity observed by other workers at elevated temperatures.

11. We have shown that the temperature coefficients generally increase with the dilution, not only in aqueous solutions but also in the non-aqueous solutions thus far studied.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1906.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF BROMINE ON DIMETHYLANILINE.

[SECOND PAPER.]

BY C. LORING JACKSON AND LATHAM CLARKE.

In the year 1904 Dr. K. Fries published the first account[1] of an extended research on the action of bromine on aromatic amines. We had been studying the action of bromine on dimethylaniline for some months before the appearance of this paper and, as our observations led us to believe that our products belonged to a different class from the perbromides described by Dr. Fries, we decided that we could finish and publish our work without approaching too near to the field reserved by him. When Dr. Fries received our paper[2] he repeated our experiments and, although he followed our directions most carefully, obtained from them only a hydrobromide and perbromides identical with those prepared in his earlier work. With the greatest kindness he then wrote us an account of his results, and pointed out that they indicated we were mistaken in the constitution ascribed to our compounds. These are given in the following table, in which the first column gives the formulas as determined by us and the second the

[1] Ber. d. chem. Ges., **37**, 2338 (1904). For a full account of his work see "Habilitationschrift," Marburg, 1905, or Ann. Chem. (Liebig), **346**, 128 (1906).

[2] THIS JOURNAL, **34**, 261 (1905).

formulas of the substances obtained by Dr. Fries when following the directions for our experiments:

Jackson and Clarke.	Fries.
1. $Br_2C_6H_3N(CH_3)_2$	$C_6H_4BrN(CH_3)_2.HBr$
2. $Br_2C_6H_3N(CH_3)_2Br_2$	$C_6H_4BrN(CH_3)_2.HBr_3$
3. $Br_2C_6H_3BrN(CH_3)_2Br_2$	$C_6H_3Br_2N(CH_3)_2.HBr_3$

In our formulas the bromine is added to the benzene ring or the nitrogen of the amino group, in his the added bromine is attached to the bromine of the hydrobromide, making perbromides.

Our formulas depended on two observations, of which the most important was that when crystals of the first substance were mixed with ethyl bromide they became oily and, after the two liquids had stood in contact for a few minutes, crystals began to appear on the surface of the oil, which, after some hours, was almost completely converted into white, flat prisms mixed with a small amount of red substance. These crystals were dried on a porous plate and analyzed without further purification.

0.0663 gram substance gave 0.0955 gram AgBr.

	Calculated for $Br_2C_6H_3N(CH_3)_2.C_2H_5Br$.	Found.
Br	61.54	61.27

Dr. Fries, on repeating the treatment of dimethylaniline with bromine, molecule for molecule, which gave us substance No. 1, obtained, even at —20°, only the hydrobromide of parabromdimethylaniline, $C_6H_4BrN(CH_3)_2.HBr$, identical with that made from hydrobromic acid and parabromdimethylaniline. This naturally led him to the conclusion that we had also obtained this substance and that our analysis of

$$Br_2C_6H_3N(CH_3)_2.C_2H_5Br$$

given above—the only real proof that the substance had our formula—was due to some experimental mistake. He supported this view by pointing out that our analysis was made with a very small amount of substance, 0.0663 gram, and that our supposed quaternary ammonic bromide,

$$Br_2C_6H_3N(CH_3)_2.C_2H_5Br,$$

was decomposed by water instead of dissolving in it unaltered, as would be expected. If his view were correct, and our substance was a substituted hydrobromide, the further action of bromine upon it would give the perbromides 2 and 3 in the second column of the table, instead of the addition compounds, which we thought we had obtained (column 1).

Accordingly, after receiving Dr. Fries' letter, we repeated our experiments on the action of bromine on dimethylaniline, molecule for molecule, and, in the first two preparations, obtained parabromdimethylaniline, $C_6H_4BrN(CH_3)_2$, recognized by its melting point, 55°; but our third experiment gave instead a viscous product, a portion of which, on treatment with ethyl bromide, yielded white crystals, and these, after drying on a porous plate, gave the following result on analysis:

0.3505 gram substance gave 0.5004 gram AgBr.

	Calculated for $Br_2C_6H_3N(CH_3)_2.C_2H_5Br$.	Found.
Br	61.54	60.75

This, by confirming our earlier analysis given above, and proving that this product is the quaternary ammonic bromide, disposes of Dr. Fries' suggestion that the mother substance was $C_6H_4BrN(CH_3)_2.HBr$, which could give no such product.

Although the differences in properties between Dr. Fries' hydrobromide, $C_6H_4BrN(CH_3)_2.HBr$, and our benzdibromide, $Br_2C_6H_3N(CH_3)_2$, are not great enough to prove alone that the substances are different, they are sufficient to support the proof derived from the action of ethyl bromide. Thus, our substance gives a reddish-brown color with a chloroform solution of quinone, whereas $C_6H_4BrN(CH_3)_2.HBr$ gives none, and the melting point of our crystals was 82°, whereas the hydrobromide melts at 105°, and, although it melts in the crude state at 80°–90°, according to Dr. Fries, it seems hardly probable that such good crystals as those used by us should melt 20° below the proper temperature.

The compound $Br_2C_6H_3N(CH_3)_2.C_2H_5Br$ was decomposed by water, as observed by us previously, but we were unable to study this phenomenon as we wished, because we did not succeed in obtaining the benz-3,4-dibromide of dimethylaniline

again, 5 additional attempts to make it giving only the hydrobromide of parabromdimethylaniline, as in the experiments of Dr. Fries. This decomposition of the quaternary ammonic bromide by water is not, however, so strange as appears at first sight. Dr. Fries[1] has shown that orthoparadibromdimethylaniline does not combine with methyl iodide to form a quaternary ammonic iodide, nor could he obtain an addition even by the use of dimethyl sulphate. It would be expected, therefore, that the quaternary ammonium derivative of our substance, which also contains 2 atoms of bromine, would be so unstable as to be decomposed by water.

The remainder of the benz-3,4-dibromide of dimethylaniline, made in our third preparation, was used in testing the second observation on which the constitution of our compounds depends. For this purpose it was converted by the further action of bromine into the compound $Br_3C_6H_1BrN(CH_3)_2Br_2$, No. 3 column 1 of the table, which, according to our earlier experiments, gave with sodic acetate and acetic acid only orthoparadibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2$, whereas Dr. Fries' perbromide, $C_6H_3Br_2N(CH_3)_2.HBrBr_2$, No. 3 column 2, gives[2] a mixture of orthoparadibromdimethylaniline and tribrommonomethylaniline, $C_6H_2Br_3NHCH_3$. Upon treating our new sample of the Br_6 compound with anhydrous sodic acetate, in acetic acid, an oily product was obtained which was dissolved in acetone and saturated with gaseous hydrobromic acid, the precipitate formed melted, without recrystallization, at 110°. The filtrate from this precipitate was freed from acetone by evaporation, and the residue also melted, without recrystallization, at 110°. As the orthoparadibromdimethylaniline hydrobromide, $C_6H_3Br_2N(CH_3)_2.HBr$, melts at 110° and the tribrommethylaniline hydrobromide, $C_6H_2Br_3NHCH_3.HBr$, at 202°, this experiment shows that none of the latter substance was present and, consequently, that our compound containing Br_6 is different from Fries' perbromide with a similar composition. Our later experiments, therefore, have established the accuracy of the two observations, on which the constitution of our 3 addition products rests.

[1] "Habilitationschrift," p. 67. Ann. Chem. (Liebig), 346, 190.
[2] "Habilitationschrift," p. 75. Ann. Chem. (Liebig), 346, 199.

The most interesting result of this later work is that a mixture of dimethylaniline bromine and chloroform may give 2 entirely different products, when there is no apparent difference in the conditions of the reaction; thus, sometimes the addition product, $Br_2C_6H_5N(CH_3)_2$, was formed as in our earlier and one of our later experiments; at other times the substitution product, $C_6H_4BrN(CH_3)_2.HBr$, as in Dr. Fries' work and 5 of our later experiments.

In the following consideration of the conditions of these reactions we are able to show that most of them did not cause this variation in the results. It could not be due to slight differences in the purity of the dimethylaniline or the bromine, as all of our 8 later experiments were tried with the same materials, and 7 yielded the substitution 1 the addition product. The chloroform used in all these experiments also came from the same specimen, but, as it was allowed to stand over calcic chloride during the work, the samples used in the last preparations may have been drier than those used for the earlier ones. In fact, in our first 2 preparations, the product was parabromdimethylaniline, due, perhaps, to the presence of some water; in the third the addition product was formed; and in the 4th, 5th, 6th and 8th, when the solvent was thoroughly dry, parabromdimethylaniline hydrobromide. It was possible, therefore, that the intermediate amount of moisture still present in Experiment 3 might have been the cause of the formation of the addition product. This theory seems improbable on its face, because the presence of water, with its strong attraction for hydrobromic acid, should promote substitution rather than addition, but we thought it important enough to test experimentally and, accordingly, experiment 6 was tried with the dry chloroform, experiment 7 with the same chloroform, to which a little washed chloroform had been added in order to make it slightly moist. As both these experiments gave parabromdimethylaniline hydrobromide, the difference in behavior can hardly be due to traces of moisture.

If the difference depended on a gradual decomposition of the chloroform during the series of experiments, those tried at first

would have given one result, those later the other, but, in fact, both the first and last preparations gave substitutions, the addition occurring in the third experiment. It would seem, therefore, that this possible cause must be rejected. We may add that the chloroform was kept in the dark and showed no sign of decomposition so far as one could tell by its odor.

The results cannot be due to differences in the length of the action, as it was essentially the same in all cases; nor to differences in the intensity of the sunlight, as the addition compound could also be obtained in diffused daylight; nor to differences in temperature, as Dr. Fries obtained substitution at a temperature of —20°. The proportion of the two reagents also did not influence the result, as we have obtained additions with 1, 2 or 3 molecules of bromine to each molecule of dimethylaniline.

We have been able to find only one possible cause for these differences, which has not been eliminated in the previous discussion, but, as our inability to make the addition products at present has prevented us from testing this hypothesis experimentally, we would mention it only as an indication of the direction in which future experiments will be tried in this laboratory. This hypothesis is that the air of a laboratory, in which hydrobromides or perbromides have been made, becomes filled with these substances in the form of impalpable dust, which inoculates the solutions and thus leads to the formation of substitution instead of addition products. This would explain the impossibility of obtaining additions in Dr. Fries' laboratory, and the facts that our first experiments led to additions as the rule, but, after we had made a number of perbromides, it became increasingly difficult to obtain addition products, and in our last experiments in only one case out of eight was there addition. Arrangements have been made to test experimentally the possibility of such inoculations by minute quantities of a substance,[1] and we hope in this way to arrive at a real knowledge of the cause of these strange differences in behavior.

CAMBRIDGE, MASS.,
June 1, 1906.

[1] Cf. Ostwald: Z. physik. Chem., 22, 289.

REVIEWS.

A SHORT MANUAL OF ANALYTICAL CHEMISTRY, Qualitative and Quantitative,—Inorganic and Organic. By JOHN MUTER, PH.D., F.R.S.E., F.I.C., F.C.S., etc. Fourth American edition, illustrated. The chapters relating to the analysis of drugs being based upon the eighth revision (1905) of the United States Pharmacopœia. Philadelphia: P. Blakiston's Son & Co. 1906. Price, $1.50.

The appearance of a new edition of this well-known manual of analysis for pharmacists and physicians shows that it is a favorite. It is deservedly so. In brief, compact form the book treats of the detection of metals, the detection and separation of acids, of qualitative analysis and quantitative analysis, volumetric and gravimetric, of organic analysis, of special processes for the analysis of air, water, food, drugs and urine, and of gas analysis.

The author says that the chapters on gravimetric and gas analysis are only introductory; with these exceptions the treatment is remarkably complete, though purely empiric. It is not suited to students of chemistry, but is well adapted to those who, with a slight knowledge of chemistry, need reliable instruction in analysis as a tool of their profession. E. R.

CHEMISTRY OF THE PROTEIDS. By GUSTAV MANN, M.D., B.Sc. University Demonstrator of Physiology, Oxford. Based on PROFESSOR OTTO COHNHEIM'S "Chemie der Eiweisskörper." London: Macmillan & Co. 1906. pp. 606. Price, $3.25.

This work consists largely of a translation of Cohnheim's "Chemie der Eiweisskörper." The author has introduced a considerable quantity of new matter, especially in the part dealing with colloidal solution, where he frequently refers to his book on "Physiological Histology." He attaches too much chemical significance to his histological work. Many of his expressions may cause some confusion if used by students; thus, he repeatedly refers to the decomposition products of the proteids as "dissociation products." Such statements as the following occur throughout the book: In the preface the author states, "A new view has been advanced, namely, that so-called neutral salts are, as a matter of fact, not neutral, for it is their very want of neutrality which allows them to dissolve in water, and which also enables them to dissolve globulins or to keep these compounds in solution." For this reason the reviewer thinks it is not a desirable book to be placed in the hands of the average student. It contains a good bibliography, however, and is a handy work for the specialist who can overlook such errors as would confuse and mislead a beginner. A. S. L.

THE DYNAMICS OF LIVING MATTER. By JACQUES LOEB, Professor of Physiology in the University of California. The Columbia University Press: The Macmillan Company, Agents. 1906. pp. 233. Price, $3.00.

To any one who has followed the beautiful experiments of Loeb on artificial parthenogenesis, this volume will be most welcome. The author states in his preface that this book "owes its origin to a series of 8 lectures delivered at Columbia University in the spring of 1902." An idea of the scope of the book can be gained by brief reference to the chapter headings. These are: Concerning the General Chemistry of Life Phenomena; The General Physical Constitution of Living Matter; On Some Physical Manifestations of Life; The Rôle of Electrolytes in the Formation and Preservation of Living Matter; The Effects of Heat and Radiant Energy upon Living Matter: Heliotropism; Further Facts Concerning Tropism and Related Phenomena; Fertilization; Heredity; On the Dynamics of Regenerative Processes.

This book is of interest to the chemist and physicist, as well as the biologist; since, as the author points out, "To-day every one who is familiar with the field of chemical biology acknowledges the fact that the chemistry of living matter is not specifically different from the chemistry of the laboratory." And again, "The phenomena which allow us to discriminate between dead and living matter are physical processes, *e. g.*, in higher animals, the contraction of the heart, the respiratory and other muscular motions. If the chemical process in living matter and the physical changes they bring about in the colloids were entirely known, the physical manifestations of life would also be clear to us."

It is well known that Loeb is one of the pioneers in introducing physical chemistry into physiology, and his chapter on the "Rôle of Electrolytes in the Formation and Preservation of Living Matter" is of special interest to physical chemists. The significance of physical chemistry for physiology and its direct bearing on that science are shown by the following sentence alone: "Not only the life of the aquatic animals, but the life of every cell is passed in a solution of electrolytes."

The chapter to which we naturally turn with greatest interest is that which has to do with "Fertilization," since it is especially in this field that Loeb has done so much, and such brilliant work. It is well known that Loeb has caused the unfertilized eggs of sea urchins to develop, by simply placing them in sea-water made more concentrated by the addition of sodium chloride, and has studied the difference between the larvae thus produced and those resulting from eggs fertilized

normally by means of sperm. It would lead too far, in the present connection, to discuss in detail these elaborate investigations; suffice it to quote the following sentence near the close of this chapter: "I am inclined to believe that the direct and essential effect of the spermatozoön and the methods of artificial parthenogenesis is the starting of a definite chemical process."

To one who is interested in such problems primarily from the purely chemical and physical side, it seems that this work of Loeb opens an entirely new field. H. C. J.

CHEMISTRY OF THE ALBUMENS. By S. B. SCHRYVER, D.Sc., PH.D., Lecturer in Physiological Chemistry to University College, London. Published under the auspices of the University of London. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 192. Price, $2.00.

The author here presents, in the form of 10 lectures, an excellent, readable and fairly complete resumé of the subject of proteid chemistry as it stands to-day. The great progress which has been made in this important field within the last decade is here presented in a clear, concise way which a student can readily grasp. The whole merit of the book lies in the first 8 lectures, which deal with the purely chemical aspect of the subject. The last 2 lectures consist, as the author states in the preface, of a very incomplete, critical review of the theories which have been advanced to explain the differences between living and dead matter and the nature of metabolism. In the first 8 lectures the constitution and synthesis of the decomposition products of the proteids and the synthesis of the polypeptides are dealt with in a very satisfactory manner. The work of Curtius is, however, not mentioned. The book is to be cordially recommended. A. S. L.

GRUNDRISS DER ELEKTROCHEMIE. Von DR. HANS JAHN, Professor an der Universität Berlin. Zweite umgearbeitete auflage, mit 5 abbildungen im Texte. Wien: Alfred Hölder. 1905. pp. 549. Price, M. 17.20.

Although this is called a second edition of Jahn's work, it is so thoroughly revised as to be practically a new book. The preface to the first edition contains such a number of valuable points that every one is urged to read it carefully. Not least important among the many admirable suggestions contained in this preface is that which bears upon the absolute necessity of chemists becoming familiar with the elements of higher mathematics.

As Jahn states, "Just as to-day every physicist must become familiar with mathematics in order to understand the theoretical side of his branch of science, so also, to the chemist who is not familiar with the elements of higher analysis,

the theoretical side of his subject will remain a book with seven seals.

"The progress that has been made in this direction, in recent times, is, on the whole, satisfactory. Through the introduction of physical-chemical methods into organic and inorganic chemistry, the application of mathematical analysis to these branches of natural science has been made possible.

"The elements of higher mathematics are to-day just as essential to any one who would understand the science of chemistry, in contradistinction to the great mass of more or less disconnected facts that have been accumulated during a century, as they are to the physicist, and the time is near at hand when no one can enter the field of chemistry primarily because it requires no mathematics."

The book under review is rather one of reference than a text-book. It contains 4 large sections: The Fundamental Laws of Electrochemistry; The Theory of Electrolytic Dissociation and Some of Its More Important Consequences; The Transformations of Energy in Electrochemical Processes; and Galvanic Polarization.

Whether used as a book of reference or as a text-book, this is an advanced work on electrochemistry. Its chief fault is one of omission—and the omission especially of work not published in German journals. This is becoming a common fault of German scientific treatises, and a serious fault it is. The general value of the works in which it exists is greatly lessened.

The electrochemistry by Jahn will undoubtedly find a place in every chemical and physical library, as well as in every laboratory where physical chemistry is taught. H. C. J.

DAS NEUE TECHNISCH-CHEMISCHE INSTITUT DER KÖNIGLICHEN TECHNISCHEN HOCHSCHULE ZU BERLIN UND DIE FEIER SEINER ERÖFFNUNG AM 25 NOVEMBER, 1905. Von dem Direktor des Instituts, DR. OTTO N. WITT, Geheimer Regierungsrat und Professor. Berlin: Weidmannsche Buchhandlung. 1906. pp. 38. Price, M. 2.

This is a reprint, admirably and copiously illustrated, of Professor Witt's address which has been already fully reported upon in this JOURNAL by Professor Renouf.[1] J. B. T.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1905. Issued by the Chemical Society. London: Gurney & Jackson. 1906. pp. 340. Price, 4 shillings and 6 pence, net.

The volume for 1905 maintains the standard of the volume for 1904; the statements are clear, their brevity is extreme. The last number of the Jahrbuch der Chemie, which covers the same ground, has 590 pages; as a guide for literature reference the one is as valuable as the other. R. R.

[1] THIS JOURNAL, 38, 358 (1906).